Enhanced Recollisions for Antisymmetric Molecular Orbitals in Intense Laser Fields

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The peculiarities of antisymmetric molecular orbitals are investigated in very intense linearly polarized laser pulses. For this purpose, the ionization-recollision quantum dynamics is evaluated theoretically beyond the dipole approximation. As opposed to the usual situation, the laser magnetic field component is found to strongly enhance recollision probabilities for particularly oriented antisymmetric molecular orbitals. Harmonic generation and related processes are thus allowed at high laser intensities without the common limitations by the laser magnetic field.

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Recently, molecules in intense laser fields have met growing interest [1]. On the one hand, there is a variety of phenomena known from atoms, occurring when a molecule is subjected to a laser field. These effects comprise, for instance, nonsequential double ionization [2], above-threshold ionization (ATI), and high-harmonic generation (HHG) [3]. On the other hand, there are also effects that are due to the molecular degrees of freedom, such as charge-resonance enhanced ionization [4], and effects related to the orientation of the molecule to the polarization direction of the laser field. Even simple diatomic molecules such as H_2^+ and H_2 reveal specific orientation-dependent characteristics in the ATI and HHG spectra [5]. The investigation of orientation effects and their relation to the orbital symmetry opens up an interesting field of research [6]. It was found that antisymmetric molecular orbitals have the potential to suppress ionization in the laser field [7]. Moreover, in view of the alignment techniques that are at the experimentalist's disposal [8], allowing one to bring the molecule in the preferred orientation before the interaction with the intense laser pulse, the investigation of those orientation-dependent effects is of great interest. In particular, effects due to the recollision of ionized electrons with the molecular core, such as HHG, depend sensitively on the orientation of the molecular axis during the interaction with the laser field [9]. The theoretical investigations dedicated to *molecules* in laser fields have typically been accomplished by employing the dipole approximation, except Ref. [10]. This has been justified for the parameter regimes under consideration. In contrast to this, nondipole effects for *atoms* in intense laser fields have been widely studied in recent years [3]. It turned out that in most cases the drift of electrons in the laser propagation direction, which is induced by the laser magnetic field component, has a detrimental impact on effects including, for instance, stabilization [11] and high-harmonic generation [3,12].

In this Letter, we demonstrate by carrying out the calculations beyond the dipole approximation that the electron drift induced by the laser magnetic field can be very efficiently harnessed to enhance the recollisions of electrons from molecular orbitals with mirror antisymmetry. We investigate this phenomenon by considering high-harmonic generation for the first excited electronic state of an H_2^+ model subjected to an intense linearly polarized laser pulse. This example can also be viewed as a model for antisymmetric molecular orbitals in more complex molecules. We find that, depending on the orientation of the antisymmetric molecular orbital, a tremendous enlargement of the harmonic signal is possible owing to an enhanced recollision dynamics. More generally speaking, there is evidence for recollisions, nonsequential double ionization, and high-order ATI in spite of the magnetic field drift for ultraintense pulses.

The momentum distribution of an antisymmetric orbital contains no electrons with momentum vectors within the plane of symmetry, which is in our case perpendicular to the molecular axis (see, e.g., the last paper in Ref. [6]). Therefore, when the molecular axis is orthogonal to the polarization direction of a linearly polarized laser field acting on an antisymmetric orbital, the ejected electrons exhibit a lateral drift perpendicular to the laser polarization direction. Note that this feature is valid at any time during the laser interaction within the dipole approximation for the laser field, for the antisymmetry of the electronic wave function is conserved, and, therefore, this remarkable property of the momentum wave function remains. This is depicted in Fig. 1. Because of the lateral electron drift, the recollision mechanism, on which fundamental processes such as high-order ATI and HHG are based, is significantly altered, as illustrated in Fig. 1. In the recollision model, ionized electrons move freely in the laser field. As the laser field changes its sign, the electron is accelerated towards the molecular core. In the recollision event, the electron can be scattered elastically from the core leading to the high-order ATI process, or recombination into the initial state can take place under emission of a photon. The latter possibility is the high-order harmonic generation process. But under the conditions illustrated in Fig. 1, no efficient recollision of ionized electrons with the molecular core can occur as a result of the lateral drift perpendicular to the polarization axis. In particular, the

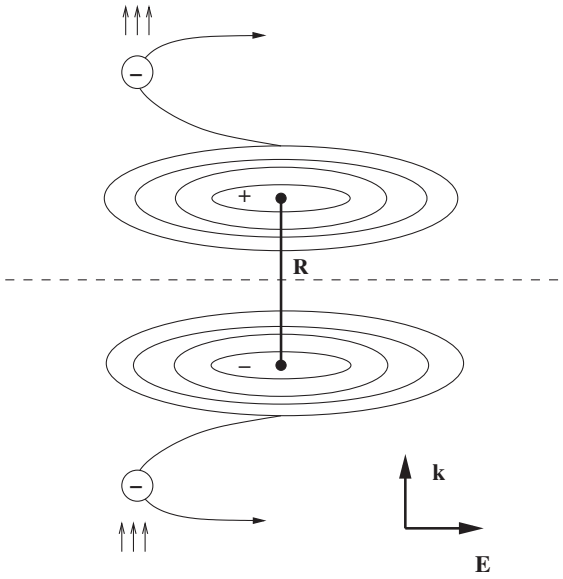

FIG. 1. Schematic diagram of an antisymmetric molecular orbital subjected to a linearly polarized laser field with polarization vector **E** and propagation direction **k** parallel to the molecular axis **R**. The dashed line symbolizes the nodal line. Within the dipole approximation, the ejected electrons cannot travel perpendicular to the molecular axis **R**. The magnetically induced electron drift helps to transfer the electron towards the molecular core, as indicated by the small arrows in the lower part of the figure.

consequence for high-harmonic generation, an important example for a recollision-dependent process, will be that the intensity of the harmonic radiation is considerably suppressed in comparison to an undisturbed recollision process. Our approach consists in the attempt to harness the electron drift in the laser propagation direction which is induced by the laser magnetic field in order to compensate the electron drift along the molecular axis that is due to the antisymmetry of the molecular orbital. This is achieved by aligning the molecule parallel to the laser propagation axis. The small arrows in the lower part of Fig. 1 indicate that the electron is transferred towards the core by the laser magnetic field. As a result, the recollision process can be accomplished more efficiently. This implies more intense generation of high harmonics. Of course, those electrons that are ejected *in* the laser propagation direction owing to the antisymmetry of the molecular orbital are steered even further away from the core by the laser magnetic field (as indicated by arrows in the upper part of Fig. 1), but as we show below, the net effect of the magnetic field will be a strong enhancement of the harmonics.

If the molecular axis is parallel to the laser polarization axis, the electron drift caused by the antisymmetry of the molecular orbital will play a minor role. In this case, the laser electric field component prevails. The electron drift in the laser propagation direction which is induced by the laser magnetic field is detrimental to the recollision in this configuration, as it has already been studied for atoms in laser fields.

To investigate the described effect in detail, we carried out numerical simulations. We solved the time-dependent Schrödinger equation [13] for the first excited antisymmetric electronic state of a 2D H_2^+ model subjected to an intense short laser pulse of linear polarization. The nuclei are clamped with an internuclear distance $R = 2$ a.u. The Hamiltonian which rules the electron dynamics reads in atomic units (a.u.):

$$H(x, y, t) = \frac{1}{2}\mathbf{p}^2 + \frac{1}{c}A_x(y, t)p_x + \frac{1}{2c^2}A_x(y, t)^2 + V_{\text{ion}}(x, y). \quad (1)$$

Here t denotes the time and c the speed of light. The x axis denotes the laser polarization direction, whereas the y axis represents the laser propagation axis. The operator $\mathbf{p} = (p_x, p_y, 0)$ represents the canonical momentum. $A_x(y, t)$ is the nonvanishing component of the vector potential $\mathbf{A} = (A_x(y, t), 0, 0)$ describing the laser pulse. The wavelength of the laser light is 248 nm (KrF laser). The envelope of the sinusoidal laser field comprises one cycle linear turn-on, four cycles with constant intensity, and one cycle linear turn-off. We perform the simulation both with and without the dipole approximation in order to study the impact of the laser magnetic field component. This means that the spatial dependence of the vector potential $A_x(y, t)$ is neglected or retained, respectively. Moreover, we carried out various simulations for different fixed angles Θ between the molecular axis and the laser electric field. The interaction of the two nuclei with the electron is described by a double-well soft-core potential:

$$V(x, y) = -\sum_{k=1,2} \frac{1}{\sqrt{(x - x_k)^2 + (y - y_k)^2 + \epsilon}},$$

where (x_1, y_1) and (x_2, y_2) are the positions of the nuclei. The soft-core parameter ϵ has been determined to 0.58 in order to reproduce the electronic eigenenergy of -0.67 a.u. of the first excited electronic state of H_2^+. This antisymmetric wave function has been obtained by means of a spectral method [15] and serves as the initial wave function for the propagation in the laser field. We note that the first excited state of H_2^+ is antibonding. The dissociation of the nuclei takes place on a much slower scale than the electronic motion. Although the nuclear motion may give rise to a small effect on the HHG spectrum [16], we neglect it here in order to concentrate on beyond-dipole effects. The initial wave function is propagated by means of the split-operator method [14] on a rectangular grid, which comprises 3072 a.u. in the laser polarization and 614 a.u. in the laser propagation directions, with 2048 time steps per optical cycle. The grid spacing is 0.15 a.u. in each direction. We compute the coherent part of the harmonic spectrum as the windowed Fourier transform of the expectation value of the dipole acceleration in the laser polarization direction.

In order to demonstrate that the drift induced by the laser magnetic field can be employed to alter the recollision process and the harmonic radiation, we performed various simulations for different angles Θ, with and without the use of the dipole approximation. Figures 2(a) and 2(b) show the harmonic spectrum obtained for a laser peak intensity of $1.4 \cdot 10^{17}$ W/cm^2 for $\Theta = 90°$ and $\Theta = 0°$, respectively. In Fig. 2(a), it becomes evident that the harmonic signal is enhanced by several orders of magnitude by the impact of the laser magnetic field. Hence, the electron drift in the laser propagation direction which is induced by the laser magnetic field improves the recollision process and increases the overlap of the recolliding electron with the initial bound wave function and other bound states repopulated during the pulse. This gives rise to an enhanced recombination process resulting in an increased harmonic emission, in accordance with the ideas depicted above. Our simulations yield that the enhancement of the harmonic signal decreases for smaller angles Θ. But for angles Θ ranging from 70° to 90°, the simulations render a considerable enhancement of the harmonic intensity for the nondipole case compared to the dipole case (for $\Theta = 70°$, the enhancement is up to 2 orders of magnitude, whereas for $\Theta = 90°$ it is up to 6 orders of magnitude). For angles in the vicinity of $\Theta = 0°$, the harmonic signal is weakened by the magnetically induced drift, as expected and described above. Figure 2(b) illustrates this for $\Theta = 0°$. There, the electron drift due to the antisymmetry of the molecular orbital is irrelevant, but signatures of two-center interference occur, as indicated by arrows. We remark that the spectra shown in Figs. 2(a) and 2(b) do not obey the common 3.17-cutoff rule [17]. This can be attributed to the rapid depopulation of the weakly bound initial state already during the rising edge of the pulse. Note that we are in the over-the-barrier, i.e., not in the tunneling, regime. This results in the alternate depletion and repopulation of the initial state. Projecting the propagated wave function onto other bound states reveals also the depletion and repopulation of these states during the pulse.

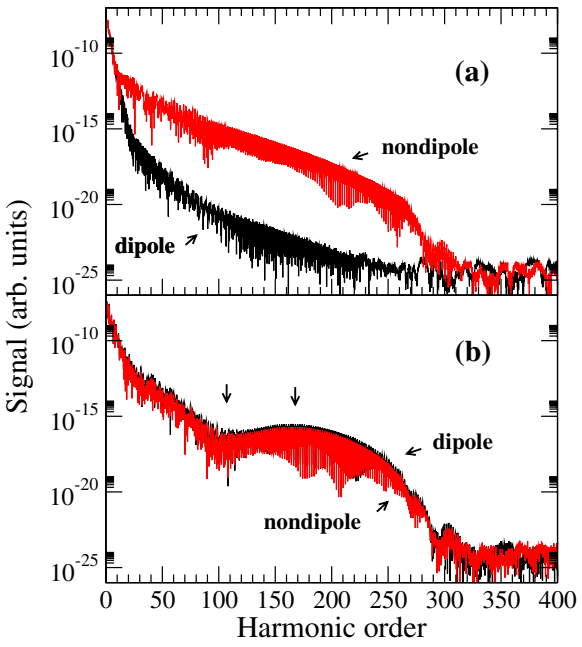

FIG. 2 (color online). Harmonic spectrum (a) for $\Theta = 90°$ and (b) for $\Theta = 0°$ at a laser intensity of $1.4 \cdot 10^{17}$ W/cm^2 and a laser wavelength of 248 nm. The black line depicts the spectrum of a computation accomplished in dipole approximation, while the red (gray) one shows the harmonic signal for a simulation performed without the dipole approximation. The arrows in (b) indicate a minimum and a maximum of a two-center interference structure.

Even for a lower laser intensity of $3.51 \cdot 10^{16}$ W/cm^2, we find that, for the antisymmetric molecular orbital investigated in this Letter, the laser magnetic field can still notably contribute to an enhancement of the harmonic signal if the angle Θ is 90°. This is illustrated in Fig. 3. A distinct enhancement of the harmonic signal is discernible. This implies that, depending on the orientation of the molecular axis, recollision effects in antisymmetric molecular orbitals are very sensitive to nondipole effects.

We now focus on the illustration of the enhancement mechanism of the recollision process. We show in Figs. 4(a) and 4(b) a snapshot of the density of the electronic wave function after 3.75 optical cycles. The simulation has been carried out in the dipole approximation for Fig. 4(a), while Fig. 4(b) has been obtained without employing the dipole approximation. Because of the rapid depopulation of the initial state, the initial wave function is not visible in the figures. Considering the symmetry of the density with regard to the nodal line ($y = 0$), one recognizes in Fig. 4(a) that the antisymmetry of the wave function is conserved. The lateral spreading of the wave packet along the molecular axis increases considerably during the interaction with the laser field; in Fig. 4(a), it extends roughly up to 150 a.u. along the y axis. In contrast, in the nondipole case in Fig. 4(b), the antisymmetry of the wave

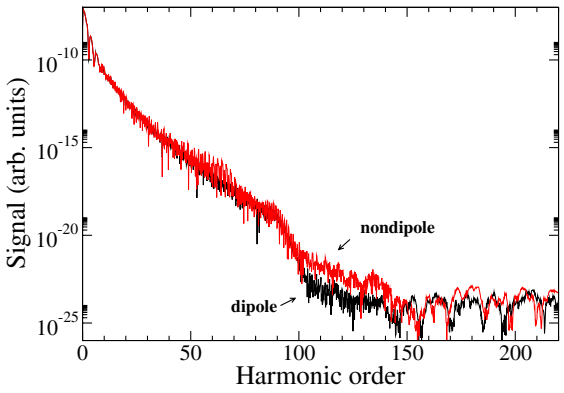

FIG. 3 (color online). Harmonic spectrum for $\Theta = 90°$ at a laser intensity of $3.51 \cdot 10^{16}$ W/cm^2 and a laser wavelength of 248 nm. The black and red (gray) lines represent the harmonic spectrum obtained with and without the application of the dipole approximation, respectively.

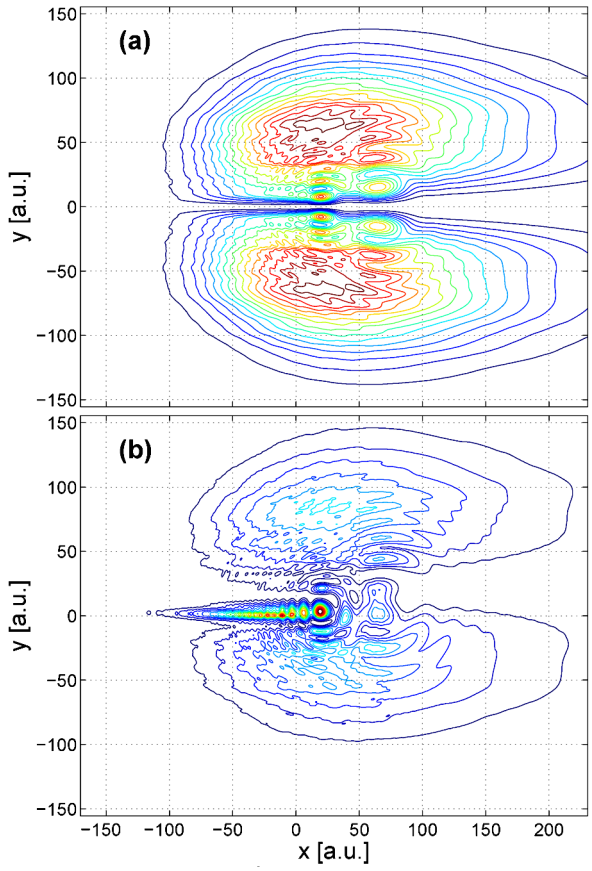

FIG. 4 (color online). Contour plot of the density of the electronic wave function for $\Theta = 90°$ and a laser intensity of $1.4 \cdot 10^{17}$ W/cm^2 (molecular axis along the y axis): (a) in the dipole approximation and (b) beyond the dipole approximation.

function is broken. A distinct drift of the wave packet towards the laser propagation direction is clearly discernible in comparison with the dipole case in Fig. 4(a). Supplementary classical Monte Carlo simulations, where the initial conditions have been determined according to the initial densities of the antisymmetric wave function and its counterpart in momentum space, do confirm the wave packet spreading depicted in Figs. 4(a) and 4(b). In addition, Fig. 4(b) illustrates a concentration of density in the vicinity of the former nodal line ($y = 0$), suggesting that bound states are repopulated during the action of the pulse. The combination of both effects leads, in comparison with the results obtained in the dipole approximation, to a highly more efficient recollision of the wave packet with the population in the core region.

In conclusion, we have seen that, depending on the orientation of the molecular axis, the electron drift induced by the laser magnetic field can be harnessed to increase the recollision probability of electrons for antisymmetric molecular orbitals. In particular, the harmonic signal can be considerably enhanced by means of the magnetically induced electron drift.

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