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High-order above-threshold ionization and high-order harmonic generation of molecule: a way of its characterization

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Abstract: We investigate high-order above-threshold ionization (HATI) and high-order harmonic generation (HHG) of diatomic molecules having different symmetries by a strong laser field using modified molecular strong-field approximation. We present our results for N_2, O_2, H_2, and Ar_2 molecules. Their initial highest occupied molecular orbitals are characterized by $3\sigma_g$, $1\pi_g$, $1\sigma_g$, and $5\sigma_u$ symmetry, respectively. By analyzing HATI and HHG spectra for different molecular orientation with respect to the laser polarization axis, and for different values of the electron or photon energies and electron emission angle, we are able to draw some conclusions about the molecular structure. The most noticeable feature of all molecular spectra is the existence of minima that are absent in the atomic case.

INTRODUCTION

Atomic and molecular nonlinear processes in a strong laser field have attracted a lot of attention in last years because of many applications in chemistry, physics, and biology. Using pump-probe techniques with ultrashort laser pulses, one can monitor molecular motion occurring on the femtosecond time scale and thus gain insight into the structure and the short-time dynamics of molecules. This concept has led to the birth of femtochemistry for which the 1999 Nobel Prize in chemistry was awarded to Ahmed Zewail (Zewail, 2000). Using femtosecond lasers in order to control motion in atoms and molecules on the femtosecond time scale was studied by Wollenhaupt, Engel, and Baumert (2005). Also, in the physics, studying of different processes in the strong laser field is of great interest for a deeper understanding of the laser-matter interaction. Some of these phenomena take place within a fraction of the laser-field cycle, which, for near-infrared pulses, is on the time scale of hundreds of attoseconds. Sub-laser-cycle rescattered electron pulses were suggested as a tool for probing the molecular dynamics (Niikura, Légaré, Hasbani, *et al.*, 2002).

In this paper we focused on two processes that play important role in strong-field physics (Lein, 2007): high-order harmonic generation (HHG) and high-order above-threshold ionization (HATI). Both processes are explained in terms of

the semiclassical three-step model: (1) the atom (molecule) is ionized, (2) the ionized electron is accelerated by the laser field and driven back to its parent ion, and (3) the ionized electron rescatters off (for HATI) or recombines with (for HHG) the parent ion and high-energy electrons or high-order harmonic photons are emitted.

In the first step of these processes, the considered system absorbs more photons from the laser field than is necessary for ionization. The electron, liberated in such a way, can go directly to the detector. We call this process the direct above-threshold ionization (ATI). Owing to the influence of the laser field, the ionized electron may also return to the parent ion (second step) and elastically scatters off it (third step), before reaching the detector. In this process, the electron can absorb many more photons from the laser field than in the direct ATI. This process was named high-order ATI (HATI). For the HHG process, in the third step, the electron recombines with the parent ion and one high-energy photon is emitted. The energy spectra of HATI and HHG processes are characterized by a plateau which manifests itself as a broad energy interval of the spectrum in which the photoelectron (HATI) or photon (HHG) yield is practically constant. These intervals are followed by abrupt cutoffs.

One of the most useful theoretical approaches based on three-step model is the strong-field approximation (SFA) (see review article by Milošević, Paulus, Bauer, *et al*., 2006). The SFA was originally formulated for the low-energy part of the ATI spectra. In order to describe high-energy plateau of the HATI spectra we have developed improved version of the SFA or ISFA (for example see Milošević, Hasović, Busuladžić, *et al.,* 2007). Within this approach we included one more interaction between the ionized electron and parent atomic ion.

While these phenomena in atomic media are well understood (see review article by Milošević and Ehlotzky, 2003, and references therein), there is a small number of papers devoted to their molecular analogs, especially for molecular HATI. Molecules are multicenter systems. As a consequence, additional two-center interferences appear in the third step, and, by analyzing the electron spectra or photon spectra, we can obtain information about the molecular structure and symmetry. The ionization can take place at any of the two or more different centers, causing interference structures in the electron spectrum, which will be presented in this paper. In fact, even direct ionization (direct ATI) without rescattering reveals the initial symmetry of the molecular system (Grasbon, Paulus, Chin, *et al*., 2001). For example, the O_2 molecule shows a suppression in the low-energy electron spectra due to its π_g symmetry, while the N_2 molecule, having σ_g symmetry, does not show such a suppression (for a more recent experimental study see work by Okunishi, Shimada, Prümper, *et al*., 2007). In the case of HHG process, the major step forward was the so-called tomographic reconstruction of molecular orbitals by Itatani, Levesque, Zeidler, *et al.* (2004) where, from the measured photon spectra at various orientations of the molecular axis, the highest occupied molecular orbital (HOMO) of N_2 was reconstructed. More details and references about molecular imaging can be found in recent review articles by Lein (2007) and by Lin, Le, Chen, *et al.,* (2010).

In this paper we gave brief review of our MSFA theory, which includes the most important results obtained for linear polarization case (Section 2). Our numerical results are presented in Section 3, and finally conclusion is given in Section 4. We used atomic system of units.

THEORY

HATI

We have developed a theory of ionization of diatomic molecules by a strong laser field within modified molecular strong-field approximation (Milošević, 2006). A diatomic molecule was considered as a three-particle system, which consists of two heavy atomic (ionic) centers and an electron. After separation of the center-of-mass coordinate, the dynamics of this system is reduced to the relative electronic and nuclear coordinates. We introduced two forms of molecular SFA, one with the field-free and other with the field-dressed initial molecular bound state.

We present here the final result for the dressed modified molecular SFA in length gauge for neutral homonuclear diatomic molecules. The rate of the ATI process with absorption of n photons from the laser field is equal to

$$w = 2\pi p_f \left| T_{fi}^{(0)}(n) \right|^2 \qquad (1)$$

where the T-matrix element $T_{fi}^{(0)}(n)$ is the Fourier transform of an expression which is given by Eq. (52) in the paper by Milošević (2006). The ground-state molecular electronic wave function is presented as linear combination of atomic orbitals (LCAO) (Atkins and Friedman, 2001; Levine, 2000), i.e.

$$\left| \Psi_s^{(0)} \right\rangle = \sum_a c_{sa} \left| \psi_a^{(0)} \right\rangle \qquad (2)$$

In our notation, the connection between the coefficients c_{sa}, depends on the symmetry of the considered molecule and is given by $c_{-1a} = s_{a\lambda} c_{1a}$, with

$$s_{a\lambda} = (-1)^{l_a - m_a} (-1)^{m_\lambda}, \qquad (3a)$$

$$s_{a\lambda} = (-1)^{l_a - m_a} (-1)^{m_\lambda + 1}, \qquad (3b)$$

for g and u symmetry, respectively. Here, m_λ is the projection of the orbital angular momentum on the internuclear axis. For example, for σ states it is m_λ=0, while for π states it is m_λ=1. The factor $(-1)^{l_a - m_a}$ comes from the inversion of the z coordinate of the second center. Using the above-described theory we reproduced key features of the most important experiment in which low-energy electrons or ATI electrons were collected (Busuladžić and Milošević, 2010).

In the previous papers (Busuladžić *et al*., 2008), we have generalized this theory to include the rescattering of the ionized electron off the parent molecular ion. Following mentioned procedure we got two terms, first of them describes the direct ATI, and it was given by $T_{fi}^{(0)}(n)$. The second term, denoted by $T_{fi}^{(1)}(n)$, that corresponds to the rescattered electrons is a very complex function and can be presented as the Fourier transform of an expression given by Eq. (22) in the paper by Busuladžić, Gazibegović-Busuladžić, Milošević, *et al*. (2008). The total rate accounts for the coherent sum of the direct term ($T_{fi}^{(0)}(n)$) and rescattering one $T_{fi}^{(1)}(n)$, (Busuladžić *et al*., 2008).

As the molecules are multicenter systems, the ionization as well as the rescattering can happen at different centers, causing interference structures in the electron spectrum. So, our matrix element T related to rescattering process can be decomposed into four terms

$$T^{(1)} = T^{++} + T^{+-} + T^{-+} + T^{--}. \quad (4)$$

The electron can tunnel out of either atom. These possibilities are denoted by superscript "+" or "–". With T^{++} (T^{--}) we denote the T-matrix contribution of the electron which, after excursion in the continuum, rescatters at the same center "+" ("–"). The terms T^{+-} and T^{-+}, correspond to the cases where the electron is ionized and rescatters off different centers. It can be shown that our matrix element is proportional to $\cos\left[\left(\vec{p}_f - \vec{k}_{st}\right)\cdot\vec{R}_0/2\right]$, regardless of the symmetry of the atomic orbital of which the considered molecular orbital consists (Busuladžić, *et al*., 2008). In the last equation $\vec{p}_f$ is the final momentum of detected electron, $\vec{k}_{st}$ is the stationary intermediate electron momentum between the ionization and rescattering (it is in the direction of the laser electric field vector) and $\vec{R}_0$ is the internuclear axis. Therefore, if we present the rescattering ionization rate in the (E_{pf}, θ) plane, we will have local minima if the condition

$$R_0\left|p_f\cos\theta - k_{st}\cos\theta_L\right| = (2m+1)\pi, \quad (5)$$

with m integer, is fulfilled. Here, θ is angle between the final momentum of detected electron and the internuclear axis, while θ_L is the angle between the internuclear axis and the laser polarization axis. This novel two-source two-rescattering-centers interference survives the focal averaging and even has been observed in experiments with unaligned molecules. Averaging over molecular orientations was considered in paper published by Milošević, Busuladžić, Gazibegović-Busuladžić, *et al*., (2009).

For elliptical polarization the destructive interference condition still holds (Busuladžić, Gazibegović-Busuladžić and Milošević, 2009; Busuladžić, Gazibegović-Busuladžić and Milošević, 2010) but one should have in mind that $\vec{k}_{st}$ is a complex solution of the saddle-point equations (Salières, Carré, Le Déroff, *et al*., 2001).

HHG

Now, we will consider HHG process on molecular targets. For a T=2π/ω -periodic laser field the rate of emission of a harmonic photon is given by (Odžak and Milošević, 2009; Odžak and Milošević, 2011)

$$w_n^{qq'} = \frac{1}{2\pi}\left(\frac{n\omega}{c}\right)^3\left|\int_0^T\frac{dt}{T}e^{in\omega t}\hat{\vec{e}}_{\vec{K}}^{\,*}\cdot\vec{d}^{\,qq'}(t)\right|^2, \quad (6)$$

where the time-dependent dipole $\vec{d}^{\,qq'}$ was given by Eq. (17) in the above-cited paper. By $\vec{e}_{\vec{K}}$ we denote the polarization vector of the emitted harmonic. As in the case of HATI one can observe interference minima in the molecular HHG spectra. Using the examples of the N_2 ($3\sigma_g$) and O_2 ($1\pi_g$) molecules, we will analyze these interference minima as well as conditions for theirs location in the HHG spectra. The returning electron wave packet recombines into the molecular orbital ($3\sigma_g$ for N_2 or $1\pi_g$ for O_2) which is a linear combination of even and odd atomic orbitals (see the next section). The corresponding partial recombination amplitudes interfere destructively for the emitted harmonic order, which is the solution of the corresponding nonlinear equation (Odžak and Milošević, 2009).

It can be shown that our matrix element is proportional to

$$\vec{K}^q\left(\vec{k}_{st},t\right)\cdot\vec{R}_0 = \begin{cases}(2j+1)\pi & \text{for } s_{a\lambda}=+1\\ 2j\pi & \text{for } s_{a\lambda}=-1\end{cases}, \quad (7)$$

where $\vec{K}^q$ is given by Eq. (B5) in paper published by Odžak and Milošević (2009) and j is an integer. Using (B5) and (C2) in the above-mentioned reference we finally obtain the following condition for the interference minima (Odžak and Milošević, 2009) for $s_{a\lambda}=+1$

$$n_{\min}^{(u,+1)} = \frac{I_P}{\omega} + \frac{(2j+1)^2\pi^2}{2\omega R_0^2\cos^2\theta_L}, \quad j=0,1,\ldots \quad (8)$$

while for $s_{a\lambda}$= -1 we have

$$n_{\min}^{(u,-1)} = \frac{I_P}{\omega} + \frac{2j^2\pi^2}{\omega R_0^2\cos^2\theta_L}, \quad j=0,1,\ldots \quad (9).$$

RESULTS AND DISCUSSION

As examples we will consider the N_2, H_2, O_2, and Ar_2 molecules. For the N_2 (H_2) molecule, the initial HOMO is $3\sigma_g$ ($1\sigma_g$) so that the factor $(-1)^{m_\lambda}=+1$ in Eq. (2a). Twelve atomic orbitals with m_a=0 will be taken into account: a=1s, 1s', 2s, 2s', 3s, 2p, 2p', 2p'', 3d, 3d', 3d'', and 4f (a=1s, 1s', 2s, 2s', 3s, 2p, 2p', 2p'', 3p, 3d, 3d', and 4f). Therefore, for s states we have $s_{a\lambda}$=1, while for p states it is $s_{a\lambda}$= -1, etc. The HOMO of the O_2 molecule is $1\pi_g$, so that $(-1)^{m_\lambda}=-1$. We choose five atomic orbitals having m_a=1: a=2p, 2p', 2p'', 3d, and 4f. For p and f states we have $s_{a\lambda}$= -1, while for d states it is $s_{a\lambda}$= 1. For Ar_2 ($5\sigma_u$) we take ten atomic orbitals with m_a=0: a = 1s, 2s, 2s', 3s, 3s', 2p, 2p', 3p, 3p', 3d. Now, for s and d states it is $s_{a\lambda}$= -1 (see Eq. 2b), while for p states we have $s_{a\lambda}$= 1. Atomic orbitals which enter LCAO are the Slater-type orbitals obtained using the Hartree-Fock-Roothaan method (Atkins and Friedman, 2001; Levine, 2000). In our calculation we use the equilibrium internuclear distance for all molecular targets: R_0=2.068 a.u. (for N_2), R_0=1.4 a.u. (H_2), R_0=2.282 a.u. (O_2), and R_0=7.2 a.u. (Ar_2). Also, the next value of the ionization potential is taken into account: I_p=15.58 eV (for N_2), I_p=16.18 eV (H_2), I_p=12.03 eV (O_2), and I_p=15.76 eV (Ar_2).

In Figure 1 we present angle-resolved electron energy spectra for the Ar_2 molecule for three different molecular orientations with respect to laser polarization axis: θ_L=0°, 45° and 90°. Laser field is linearly polarized having intensity 1.35 x 10^{14} W/cm^2 and wavelength λ=800 nm. First of all, we can observe pronounced minima in the HATI spectra, particularly in the cutoff region, in accordance with Eq. (5). For chosen laser and molecular parameters we have minima for values m=0,1,and 2 in Eq. (5). These features are visible in the upper and middle panels of the figure.

Our theoretical approach allows us to connect the rescattering contribution for particular molecular orientation with the ath molecular constituent [see Eq. (36) in reference by Busuladžić, *et al*., 2008). For example, in the case of Ar_2

molecule with a large value of R_0 the p-state contribution becomes dominant and it can be shown that the corresponding rescattering $T^{(1)}$-matrix contribution is proportional to $\cos\theta_L$, with the consequence that for θ_L=90° the rescattering plateau is absent. This is illustrated by the bottom panel of Fig. 1. This is one example of how one can obtain information about the molecular symmetry by analyzing the angle- and energy-resolved HATI spectra (Milošević *et al*., 2009).

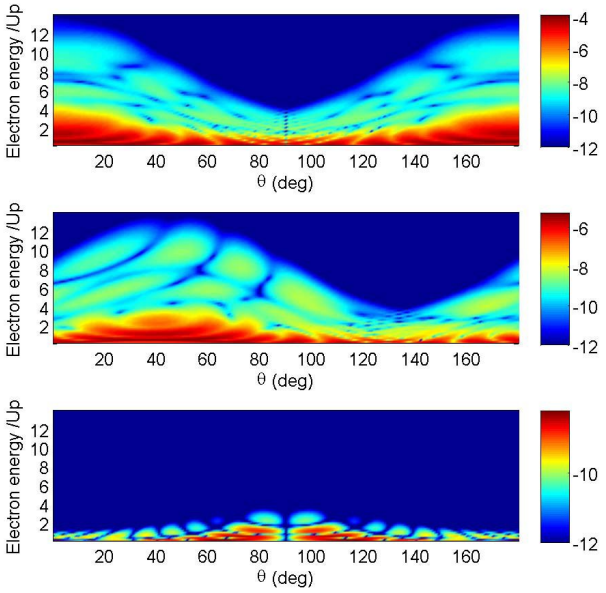

Figure 1: Logarithm of the differential ionization rate of Ar_2, coded in false colors in the (E_{pf}, θ) plane, for three different orientations of the molecular axis with respect to the polarization vector of the laser field, from the top to the bottom panel: θ_L=0°, 45°, and 90°. Intensity of the linearly polarized laser field is 1.35 x 10^{14} W/cm^2 and the wavelength is 800 nm. The electron kinetic energy E_{pf} is presented in units of U_p, where U_p is defined as the ponderomotive energy of the electron in the laser field. All HATI spectra are obtained using the dressed length-gauge modified MSFA.

It is important to stress that this novel two-source two-rescattering-centers interference has been observed in experiments with unaligned molecules (Okunishi, Itaya, Shimada, *et al*., 2009; Kang, Quan, Wang, *et al*., 2010). More precisely, the suppression remains visible in the orientation-averaged spectrum of O_2 but not of N_2 molecule. This is related with its ground state function symmetry (Okunishi, *et al*., 2009). For parallel θ_L=0° and perpendicular θ_L=90° orientations, the high-energy plateau for O_2 is entirely absent (Busuladžić *et al*., 2008), while for angles close to θ_L=0° or θ_L=90° it is few orders of magnitude lower than that of N_2. The fact that the suppression remains visible in the orientation-averaged spectrum of O_2 but not of N_2 is due to the fact that for N_2 it is filled in by contributions from small and large angles. These contributions are absent or very low for O_2. This effect is different from the suppression of ionization (direct ATI) that is well known to occur for O_2 (Grasbon, *et al*., 2001).

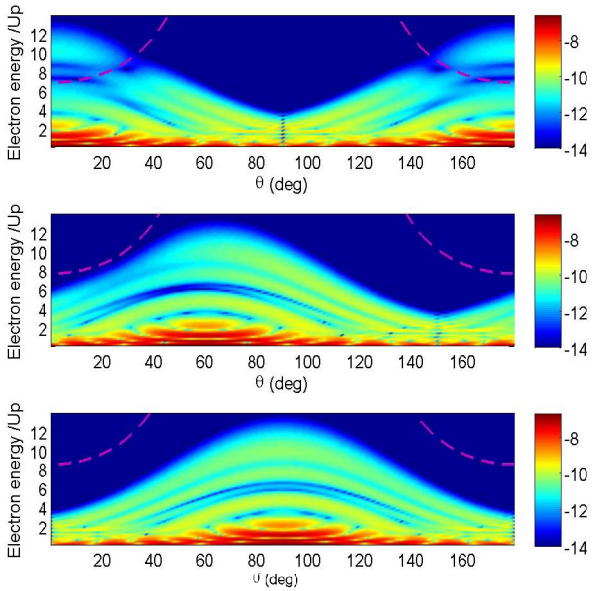

Figure 2: The same as in Fig 1, but now for H_2 molecule and for θ_L=0°, 60°, and 90°. The dashed pink curves are based on Eq. (5), (see the text).

In Fig. 2 we present angle-resolved energy spectra for the H_2 molecule for the following molecular orientations: θ_L=0°, 60°, and 90° The laser parameters are the same as in the previous figure. The spectra for θ_L=0° (top panel) and θ_L=90° (bottom panel) are symmetric with respect to θ=θ_L axis, while this symmetry is absent for θ_L=60° (middle panel). Again, for parallel orientation: θ_L=0° one can see the existence of minima that are absent in the atomic case (Busuladžić *et al*., 2008; Milošević *et al*., 2009). Now, this cannot be observed for larger values of θ_L. The reason for that is a small value of the internuclear distance between atomic centers in the hydrogen molecule. The dashed curves presented in all panels are based on Eq. (5). We can see in the middle and bottom panels that the curves go above the registered HATI spectra. In order to observe minima for larger angles for H_2 we have to increase intensity of the applied laser field. In Fig. 3 we present HATI spectrum of H_2 and perpendicular orientation (θ_L=90°) but now for the intensity 3.0 x 10^{14} W/cm^2. Value of the wavelength is not changed. For this higher intensity the minima can be observed. Moreover, our condition for interference minima gives a perfect fit of the minima position. This can be explained in the following way. For θ_L=90° the negative-parity atomic orbitals ($s_{a\lambda}$= -1) do not contribute to rescattering (Busuladžić *et al*., 2008) and the condition (5) reduces to

$$E_{p_f}\cos^2\theta = \frac{\pi^2}{2R_0^2}\ , \quad (10)$$

which allows, in principle, to determine the internuclear separation.

Because of the small value of the intenuclear separation for H_2 the suppression occurs at higher energies [see Eq. (10)]. In order to obtain the interference minima for perpendicular orientation we have to increase the intensity of the laser field.

Generally speaking, the spectra of H_2 are very similar to those of the N_2 molecule. This is because of the same type of symmetry of its HOMO. More precisely, the HOMO of N_2 is $3\sigma_g$, while the HOMO of H_2 molecule is $1\sigma_g$. Because of the different symmetry of the O_2 ground-state wave function, the corresponding spectra are very different from those of H_2 or N_2. Also, we suppose that in the orientation averaged HATI spectra of H_2 the interference structure should be masked as it was the case for N_2 molecule (Okunishi, *et al.,* 2009).

More recently, we have developed molecular low-frequency approximation (MLFA) in order to simulate a molecular HATI experiment by ultrashort laser pulses. This new approach has enabled us to explain a new type of minima which are not due to two-source double-slit destructive interference. The MLFA theory is better approximation than the MISFA (Gazibegović-Busuladžić, Hasović, Busuladžić, *et al.*, 2011).

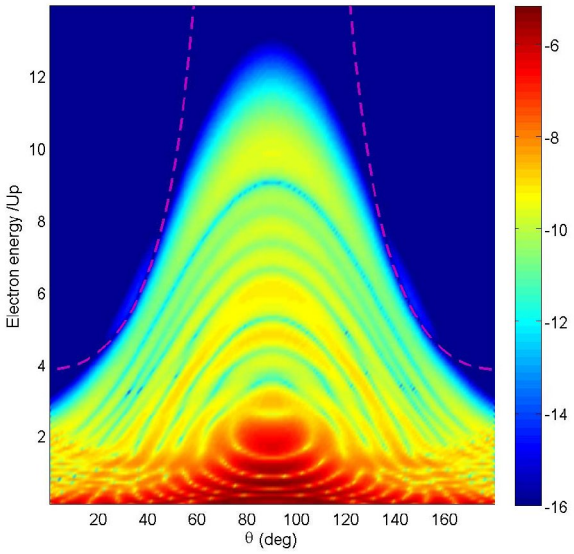

Figure 3: The same as in the bottom panel of Fig. 2, but for the intensity of 3.0 x 10^{14} W/cm^2.

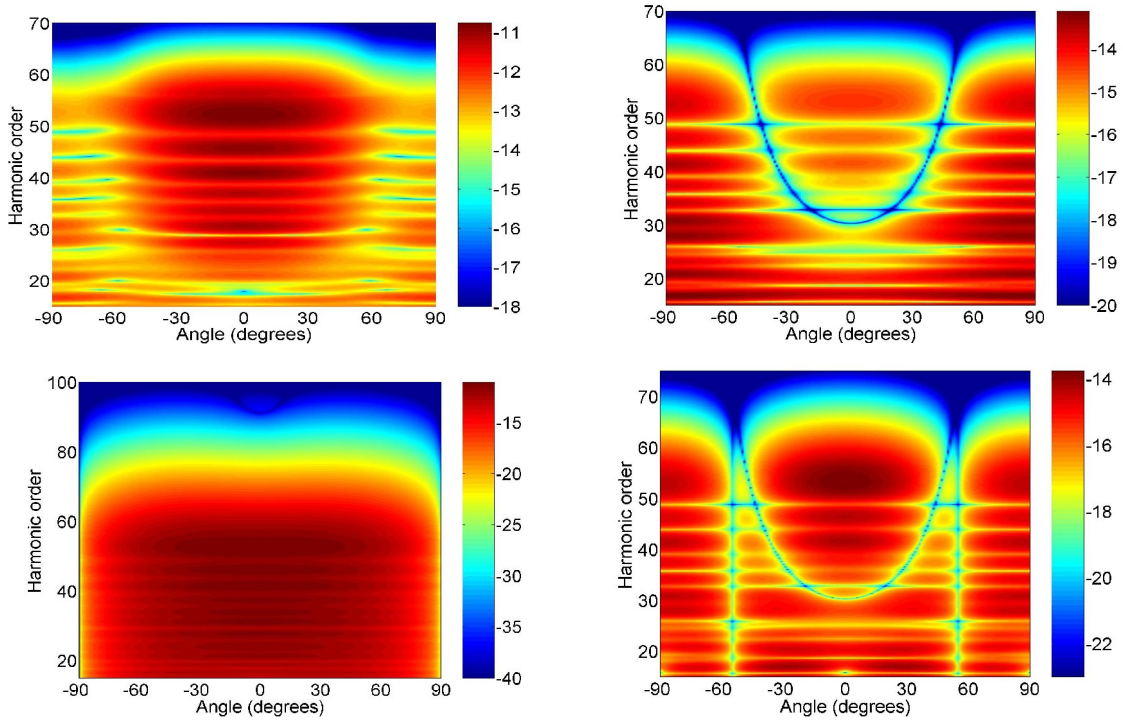

Figure 4: High-order harmonic spectra of the N_2 molecule obtained using a linearly polarized field having intensity 3.5 x 10^{14} W/cm^2 and wavelength of 800 nm. Both components of the *T*-matrix element are used in calculations. Also, the final state is undressed. Upper left panel: Contributions of *s*, *p*, and *d* atomic orbitals within LCAO are included in calculated HHG spectrum, upper right: only taking *s* atomic orbitals, bottom left: only *p* orbitals and bottom right panel: only *d* orbitals.

Now, we will present our results for molecular HHG process. In Fig. 4 we present in false color the harmonic emission rate in the plane (θ_L, n) for N_2 molecule obtained using a linearly polarized laser field having the intensity 3.5 x 10^{14} W/cm^2 and the wavelength λ=800 nm. The angle θ_L is defined as angle between the internuclear axis and the laser polarization axis. By n we denote the harmonic order. In all calculations the final state is undressed (Milošević, 2006). Clear two-center interference minima appear and these minima form a curve in the plane (θ_L, n) for all partial contributions which include only *s*, *p* or *d* atomic orbitals. These results are presented in the upper right, bottom left, and

bottom right panel, respectively. If we take only contributions of the components of the *T*-matrix element in the direction of the laser-field polarization we will have interference minima in accordance with formula (24) in work by Odžak and Milošević (2009). Corresponding results was presented in Fig. 3 (b) in the mentioned paper where one can observe minima in the harmonic spectrum. These minima are related with the relative contribution of even (*s* and *d*) and odd (*p* and *f*) atomic orbitals. The interference picture was completely different from the interference structure where we included only one type of orbitals. In the last case minima will appear in accordance with Eq. (8) for j=0 (*s* and *d* orbitals) and Eq. (9) for j=1 (*p* orbitals). These equations are special cases of Eq. (24) showed in paper by Odžak and Milošević (2009). This formula contains the ratio of the sum of the dipole matrix elements with even and odd atomic orbitals whose linear combination forms the molecular orbital from which the high harmonics are emitted. We have shown that the destructive interference of even and odd partial recombination amplitudes is responsible for the observed minima (Odžak and Milošević, 2009). In the upper left panel of Fig. 4 the interference structure is blured. Here, in our calculation we also include *T*-matrix element in the direction perpendicular to the laser polarization axis (Odžak and Milošević, 2010). This component has a big influence on the HHG spectrum of N_2 molecule that is on the interference structure appearing in the corresponding HHG spectrum. In other words, including perpendicular component of *T*-matrix element leads to washing out of clear interference minima structure (Odžak and Milošević, 2010; Odžak and Milošević, 2011).

Now, we are going to show HHG spectra of O_2. Since the main contribution to the $1\pi_g$ HOMO of the O_2 molecule comes from the *p* atomic orbitals, we expect that the interference minima will appear for higher harmonic orders, i.e., higher laser intensities are needed to observe these minima (see the upper panel of Fig. 5). The laser intensity is 5.0 x 10^{14} W/cm^2, which is higher than that used in experiment presented in Fig. 4. The wavelength is not changed. Again, only the combinations with the undressed final state lead to clear interference minima. In the total spectrum perpendicular component of *T*-matrix element was included.

Furthermore, these interference minima are very well described by Eq. (10) for j=−1 (bottom panel). In the total HHG spectrum of O_2 one can see that the influence of the perpendicular component of the *T*-matrix element is less pronounced and the interference structure is more clearly visible than in the N_2 case.

CONCLUSIONS

In this paper we have presented various numerical results for HATI and HHG of molecular systems characterized by different symmetry.

The results are obtained using our improved MSFA theory. We have predicted dramatic differences between the high-energy plateaus in the angle-resolved electron and photon spectra for different molecules. Also, the most noticeable feature of the molecular HATI and HHG spectra is the existence of minima that are absent in the atomic case. We have derived an analytical formula for their position for both considered processes. Influence of internuclear distance as well as of different atomic orbitals on the position of the minima is considered.

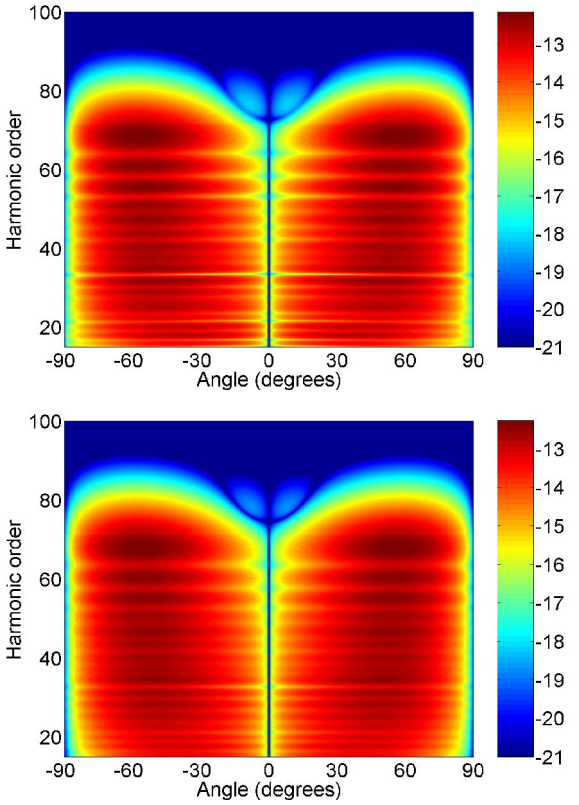

Figure 5. As in the previous figure, but now for O_2 and intensity of 5.0 x 10^{14} W/cm^2. In the upper panel we use *p*, *d*, and *f* atomic orbitals, while in the bottom panel only *p* orbitals are taken into account.

REFERENCES

Atkins, P. W., Friedman, R. S. (2001). *Molecular Quantum Mechanics*, (3rd Ed.), Oxford University Press, Oxford.

Busuladžić, M., Gazibegović-Busuladžić, A., Milošević, D. B., Becker, W. (2008). Angle-resolved high-order above-threshold ionization of a molecule: Sensitive tool for molecular characterization. *Physical Review Letters 100 (20)*, 203003, 1-4; Strong-field approximation for ionization of a diatomic molecule by a strong laser field. II. The role of electron rescattering off the molecular centers. *Physical Review A 78 (3)*, 033412, 1-11.

Busuladžić, M., Gazibegović-Busuladžić, A., Milošević, D. B. (2009). Strong-field approximation for ionization of a diatomic molecule by a strong laser field. III. High-order above-threshold ionization by an elliptically polarized field. *Physical Review A 80 (1)*, 013420, 1-8. (2010). Ellipticity dependence of high-order above-threshold ionization from aligned

diatomic molecules*, Laser Physics 20 (5),* 1001-1008.

Busuladžić, M., Milošević, D. B. (2010). Simulation of above-threshold-ionization experiment using the molecular strong-field approximation: the choice of gauge. *Physical Review A 82 (1)***,** 015401, 1-4.

Gazibegović-Busuladžić, A., Hasović, E., Busuladžić, M., Milošević, D. B., Kelkensberg, F., Siu, W. K., Vrakking, M. J. J., Lépine, F., Sansone, G., Nisoli, M., Znakovskaya, I., Kling, M. F. (2011). Above-threshold ionization of diatomic molecules by few-cycle pulses. *Physical Review A 84* (4), 043426, 1-8.

Grasbon, F., Paulus, G. G., Chin, S. L., Walther, H., Muth-Böhm, J., Becker, A., Faisal, F. H. M. (2001). Signatures of symmetry-induced quantum-interference effect observed in above-threshold-ionization spectra of molecules. *Physical Review A 63 (4)*, 041402 (R), 1-4.

Itatani, J., Levesque, J., Zeidler, D., Niikura, H., Pépin, H., Kieffer, J. C., Corkum, P. B., Villeneuve, D. M. (2004). Tomographic imaging of molecular orbitals. *Nature (London) 432 (7019)*, 867-871.

Kang, H., Quan, W., Wang, Y., Lin, Z., Wu, M., Liu, H., Liu, X., Wang, B. B., Liu, H. J., Gu, Y. Q., Jia, X. Y., Liu, J., Chen, J., Cheng, Y. (2010). Structure Effects in Angle-Resolved High-Order Above-Threshold Ionization of Molecules. *Physical Review Letters 104 (20),* 203001, 1-4.

Lein, M. (2007). Molecular imaging using recolliding electrons. *Journal of Physics B: Atomic, Molecular and Optical Physics 40 (16)*, R135-R173.

Levine, I. N. (2000). *Quantum Chemistry*, (5th Ed.), Prentice-Hall, Upper Saddle River, New Jersey.

Lin, C. D., Le, A. T., Chen, Z., Morishita, T., Lucchese, R. (2010). Strong-field rescattering physics-- self-imaging of a molecule by its own electrons. *Journal of Physics B: Atomic, Molecular and Optical Physics 43 (12),* 122001, 1-33 .

Milošević, D. B., Ehlotzky, F. (2003). Scattering and reaction processes in powerful laser fields. *Advances in Atomic, Molecular, and Optical Physics 49*, 373-532.

Milošević, D. B., Paulus, G. G., Bauer, D., Becker, W. (2006). Above-threshold Ionization by few-cycle pulses. *Journal of Physics B: Atomic, Molecular and Optical Physics 39 (14), R203*-262.

Milošević, D. B. (2006). Strong-field approximation for ionization of a diatomic molecule by a strong laser field. *Physical Review A 74 (6)*, 063404, 1-14.

Milošević, D. B., Hasović, E., Busuladžić, M., Gazibegović-Busuladžić, A., Becker, W. (2007). Intensity-dependent enhancements in high-order above-threshold ionization. *Physical Review A 76 (5)*, 053410, 1-16.

Milošević, D. B., Hasović, E., Odžak, S., Busuladžić, M., Gazibegović-Busuladžić, A., Becker, W. (2009). New results in above-threshold ionization and high-order harmonic generation of atomic and molecular systems. *Laser Physics 19 (2),* 185-190.

Milošević, D. B., Busuladžić, M., Gazibegović-Busuladžić, A., Becker, W. (2009). Strong-field approximation for high-order above-threshold ionization of randomly oriented diatomic molecules. *Chem. Phys. 366 (1-3),* 85-90.

Niikura, H., Légaré, F., Hasbani, R., Bandrauk, A. D., Ivanov, M. Y., Villeneuve, D. M., Corkum, P. B. (2002). Sub-laser-cycle pulses for probing molecular dynamics. *Nature (London) 417 (6892)*, 917-922.

Odžak, S., Milošević, D. B. (2009). Interference effects in high-order harmonic generation by homonuclear diatomic molecules. *Physical Review A 79 (2),* 023414, 1-12.

Odžak, S., Milošević, D. B. (2010). Role of ellipticity in high-order harmonic generation by homonuclear diatomic molecules. *Physical Review A 82 (2)*, 023412, 1-8; (2011). Ellipticity and the offset angle of high harmonics generated by homonuclear diatomic molecules *Journal of Physics B: Atomic, Molecular and Optical Physics 44 (12)*, 125602, 1-7.

Okunishi, M., Shimada, K., Prümper, G., Mathur, D., Ueda, K. (2007). Probing molecular symmetry effects in the ionization of N_2 and O_2 by intense laser fields. *Journal of Chemical Physics 127 (6)*, 064310, 1-4.

Okunishi, M., Itaya, R., Shimada, K., Prümper, G., Ueda, K., Busuladžić, M., Gazibegović-Busuladžić, A., Milošević, D. B., Becker, W. (2009). Two-source double-slit interference in angle-resolved high-energy above-threshold ionization spectra of diatoms. *Physical Review Letters 103 (4),* 043001, 1-4.

Salières, P., Carré, B., Le Déroff, L., Grasbon, F., Paulus, G. G., Walther, H., Kopold, R., Becker, W., Milošević, D. B., Sanpera, A., Lewenstein, M. (2001). Feynman's path-integral approach for intense-laser-atom interactions. *Science 292 (5518)*, 902-905.

Wollenhaupt, M., Engel, V., Baumert, T. (2005). Femtosecond laser photoelectron spectroscopy on atoms and small molecules: Prototype studies in quantum control- *Annual Review of Physical Chemistry 56*, 25-56.

Zewail, A. H. (2000). Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. *J. Phys. Chem. A 104 (24),* 5660–5694.

Summary/Sažetak

U ovome radu istražujemo procese jonizacije iznad praga višeg reda (eng. HATI) i generacije viših harmonika (eng. HHG) na dvoatomskim molekulama karakterisanih različitom simetrijom u jakom laserskom polju. Pri analizi je korištena modifikovana molekularna aproksimacija jakog polja (eng. MSFA). U radu smo predstavili rezultate za nekoliko molekula: N_2, O_2, H_2 i Ar_2 . Njihove najviše zaposjednute molekularne orbitale (eng. HOMO) su karakterisane $3\sigma_g$, $1\pi_g$, $1\sigma_g$ i $5\sigma_u$ simetrijom, respektivno. Analizirajući dobivene HATI i HHG spektre za različite orijentacije pomenutih molekula u odnosu na osu polarizacije laserskog polja, te za različite vrijednosti energije emitovanih elektrona i fotona, kao i odgovarajućeg ugla emisije, moguće je izvesti određene zaključke o samoj strukturi posmatranih molekula. Najznačajnija crta dobivenih molekularnih spektara su minimumi koji su odsutni atomskom slučaju.