

PAPER • OPEN ACCESS

## High-order harmonic generation by polyatomic molecules

To cite this article: S Odžak *et al* 2017 *J. Phys.: Conf. Ser.* **826** 012007

View the [article online](#) for updates and enhancements.

You may also like

- [Trilobites, butterflies, and other exotic specimens of long-range Rydberg molecules](#)  
Matthew T Eiles
- [The scientific career of V S Letokhov \(10 November 1939–21 March 2009\)](#)  
Victor I Balykin
- [Polyatomic molecules as quantum sensors for fundamental physics](#)  
Nicholas R Hutzler



**245th ECS Meeting**  
San Francisco, CA  
May 26–30, 2024

**PRiME 2024**  
Honolulu, Hawaii  
October 6–11, 2024

Bringing together industry, researchers, and government across 50 symposia in electrochemistry and solid state science and technology

Learn more about ECS Meetings at  
<http://www.electrochem.org/upcoming-meetings>

 Save the Dates for future ECS Meetings!

# High-order harmonic generation by polyatomic molecules

S Odžak<sup>1</sup>, E Hasović<sup>1</sup> and D B Milošević<sup>1,2,3</sup>

<sup>1</sup> Faculty of Science, University of Sarajevo, Zmaja od Bosne 35, 71000 Sarajevo, Bosnia and Herzegovina

<sup>2</sup> Max-Born Institut, Max-Born Strasse 2a, 12489 Berlin, Germany

<sup>3</sup> Academy of Sciences and Arts of Bosnia and Herzegovina, Bistrik 7, 71000 Sarajevo, Bosnia and Herzegovina

E-mail: senad.odzak@pmf.unsa.ba

**Abstract.** We present a theory of high-order harmonic generation by arbitrary polyatomic molecules based on the molecular strong-field approximation (MSFA) in the framework of the  $S$ -matrix theory. A polyatomic molecule is modeled by an  $(N + 1)$ -particle system, which consists of  $N$  heavy atomic (ionic) centers and an electron. We derived various versions (with or without the dressing of the initial and/or final molecular state) of the MSFA. The general expression for the  $T$ -matrix element takes a simple form for neutral polyatomic molecules. We show the existence of the interference minima in the harmonic spectrum and explain these minima as a multiple-slit type of interference. This is illustrated by numerical examples for the nitrous oxide ( $N_2O$ ) molecule exposed to strong linearly polarized laser field.

## 1. Introduction

With the advent of high-power lasers, many interesting nonlinear phenomena have been observed when exposing atoms and molecules to strong laser fields (see review articles [1, 2] and references therein). High-order harmonic generation (HHG) is a unique highly nonlinear process which has attracted attention of experimental and theoretical physicists over the past three decades. As a source of coherent extreme ultraviolet and soft x-ray radiation, this process has important applications in time-resolved spectroscopy and attoscience [3, 4, 5, 6, 7]. HHG may be described by the so-called three-step model [8]. In the first step, the considered molecular target absorbs more photons from the laser field than is necessary for ionization. Influenced by the laser field, the released electron may return to the parent molecular ion (the second step). In the third step, the electron recombines with the parent ion and one high-energy photon is emitted.

HHG carries information about the atomic or molecular targets, like internuclear distance of diatomic molecules or symmetry and the shape of the highest occupied molecular orbital (HOMO) of simple linear molecules [9, 10]. One powerful method to probe the structure of diatomic molecular targets is to analyze characteristic minima in the HHG spectra caused by the two-center interference of returning electron wave packet. The interference minima are first theoretically investigated for the simplest diatomic molecules  $H_2^+$  and  $H_2$  [11, 12, 13]. The experimental observation of the minima was first achieved for aligned  $CO_2$  molecules [14, 15]. While the position of the minima can be determined by a simple interference formula for diatomic molecules, the case of polyatomic molecules is considerably more complex. In [16, 17] a general



interference minima condition, which is valid for arbitrary homonuclear diatomic molecules, is derived and tested.

The HHG process for polyatomic molecules was analyzed experimentally in [18, 19, 20, 21, 22, 23, 24, 25, 26]. From a theoretical point of view, numerical solution of the time-dependent Schrödinger equation is not practical for polyatomic molecules. Therefore, most calculations of HHG spectra for polyatomic molecules are performed using approximate methods like strong-field approximation [27] or quantitative rescattering theory [24]. In this paper we present the molecular strong-field approximation (MSFA) and apply it to calculate and analyze HHG spectra of nitrous oxide molecule ( $\text{N}_2\text{O}$ ).

## 2. Theory of molecular HHG

The MSFA theory is based on our previous work [27]. A polyatomic molecule is considered as a system of  $N$  atomic (ionic) centers and an electron which can be freed under the action of the laser field with the electric field vector  $\mathbf{E}(t)$  in the molecular HHG process. The Hamiltonian of this system, in the dipole approximation and the length gauge, can be written in the form

$$H = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2m_k} + \frac{\mathbf{p}_e^2}{2m_e} + V(\mathbf{r}_e, \mathbf{r}_1, \dots, \mathbf{r}_N) - \mathbf{E}(t) \cdot \left( e\mathbf{r}_e + \sum_{k=1}^N e_k\mathbf{r}_k \right), \quad (1)$$

where  $\mathbf{p}_k$ ,  $\mathbf{r}_k$ ,  $m_k$ , and  $e_k$ , are, respectively, the momenta, coordinates, masses, and charges of atoms (ions), while  $\mathbf{p}_e$ ,  $\mathbf{r}_e$ ,  $m_e$ , and  $e$  are the momentum, coordinate, mass, and charge of the electron ( $m_e = 1$  and  $e = -1$  in the atomic units). It is convenient to introduce the Jacobi coordinates and to replace the system of  $N + 1$  coordinates  $\mathbf{r}_k$  ( $k = 1, \dots, N$ ),  $\mathbf{r}_e$ , with the system of  $N$  relative coordinates  $\mathbf{R}_k$ ,  $k = 1, \dots, N$ , and the center-of-mass coordinate  $\mathbf{R}_{\text{c.m.}}$ . In the new coordinates, the Hamiltonian of our system can be written in the form

$$H = \frac{\mathbf{P}_{\text{c.m.}}^2}{2M} + \sum_{k=1}^N \left[ \frac{\mathbf{P}_k^2}{2\mu_k} + V_k(\mathbf{r}_e - \mathbf{r}_k) \right] + V_C(\{\mathbf{R}\}) - \mathbf{E}(t) \cdot \left( \tilde{e}_{\text{c.m.}}\mathbf{R}_{\text{c.m.}} + \sum_{k=1}^N \tilde{e}_k\mathbf{R}_k \right), \quad (2)$$

where the laser-free interaction  $V(\mathbf{r}_e, \mathbf{r}_1, \dots, \mathbf{r}_N)$  is written as the sum of all electron- $k$ th molecular center potentials  $V_k(\mathbf{r}_e - \mathbf{r}_k)$  and the potential energy of these centers  $V_C(\{\mathbf{R}\})$ . The set of  $(N - 1)$  relative coordinates of atomic (ionic) centers is denoted by  $\{\mathbf{R}\} \equiv (\mathbf{R}_1, \dots, \mathbf{R}_{N-1})$ . The reduced masses are determined by the following expressions

$$\mu_j = \frac{m_{j+1}M_j}{M_{j+1}} = \lambda_j m_{j+1} = \kappa_{j+1} M_j, \quad j = 1, \dots, N, \quad (3)$$

where  $M_j = \sum_{k=1}^j m_k$ ,  $\lambda_j = M_j/M_{j+1}$  and  $\kappa_j = m_j/M_j$  while  $\mathbf{P}_{\text{c.m.}} = \sum_{k=1}^{N+1} \mathbf{p}_k$  and  $\tilde{e}_{\text{c.m.}} = \sum_{k=1}^{N+1} e_k$  are the momentum and charge of the center of mass (we introduced the notation  $\mathbf{p}_{N+1} = \mathbf{p}_e$  and  $e_{N+1} = e$ ). The relative momenta and charges are given by ( $j = 1, \dots, N$ )

$$\mathbf{P}_j = \lambda_j \mathbf{p}_{j+1} - \kappa_{j+1} \sum_{k=1}^j \mathbf{p}_k, \quad \tilde{e}_j = \lambda_j e_{j+1} - \kappa_{j+1} \sum_{k=1}^j e_k. \quad (4)$$

For a  $T = 2\pi/\omega$ -periodic laser field the rate of emission of a harmonic photon having the frequency  $\omega_{\mathbf{K}} = n\omega + E_{\text{ei}}(\{\mathbf{R}\}) - E_{\text{ef}}(\{\mathbf{R}\})$ , wave vector  $\mathbf{K}$ , and the polarization  $\hat{\mathbf{e}}_{\mathbf{K}}$ , into a solid angle  $d\Omega_{\hat{\mathbf{K}}}$ , is given by [in atomic units (au)] [28]

$$w_n^{q'q} = \frac{1}{2\pi} \left( \frac{n\omega}{c} \right)^3 \left| T_n^{q'q} \right|^2, \quad (5)$$

where the  $T$ -matrix element is

$$\mathbf{T}_n^{qq'} = \int_0^T \frac{dt}{T} e^{in\omega t} \mathbf{d}_{\text{fi}}^{qq'}(t) = T_n^{qq'} \hat{\mathbf{e}}_{\mathbf{K}} = \sum_{\xi=x,y,z} T_{n\xi}^{qq'} \hat{\mathbf{e}}_{\xi}. \quad (6)$$

The time-dependent dipole matrix element  $\mathbf{d}_{\text{fi}}^{qq'}(t)$  can be calculated within the strong-field approximation, fixed-nuclei approximation and solving the integral over the intermediate electron momentum  $\mathbf{k}$  by the saddle-point method, as it was done in [27], with the final result

$$\begin{aligned} \mathbf{d}_{\text{fi}}^{qq'}(t) &= -i \left( \frac{2\pi}{i} \right)^{3/2} \int_0^\infty \frac{d\tau}{\tau^{3/2}} e^{i[S_{\mathbf{k}_{\text{st}}}(t') - S_{\mathbf{k}_{\text{st}}}(t) + E_{\text{ei}}\tau]} \\ &\times \sum_{l=1}^N \sum_a c_{la} \eta_q(\boldsymbol{\rho}_l, t) \langle \psi_a | \tilde{e}_N \mathbf{r} + \boldsymbol{\rho}_{C_l} | \mathbf{k}_{\text{st}} - \tilde{e}_N \mathbf{A}(t) \rangle \\ &\times \sum_{j=1}^N \sum_{a'} c_{ja'} \eta_{q'}^*(\boldsymbol{\rho}_j, t') \langle \mathbf{k}_{\text{st}} - \tilde{e}_N \mathbf{A}(t') | (\tilde{e}_N \mathbf{r} + \boldsymbol{\rho}_{C_j}) \cdot \mathbf{E}(t') | \psi_{a'} \rangle. \end{aligned} \quad (7)$$

Integration in the previous equation is performed over the travel time  $\tau = t - t'$ , while the quasiclassical action is given by  $S_{\mathbf{k}}(t) = \frac{1}{2} \int_{-\infty}^t dt' [\mathbf{k} - \tilde{e}_N \mathbf{A}(t')]^2$  and is calculated at the stationary momentum  $\mathbf{k}_{\text{st}} = \tilde{e}_N \int_{t-\tau}^t \mathbf{A}(t') dt' / \tau$  where  $\mathbf{A}(t) = -\int_{-\infty}^t \mathbf{E}(t') dt'$ . The ionization (recombination) matrix element is obtained by expanding the molecular orbitals as a linear combination of atomic orbitals  $|\psi_a\rangle$  with expansion coefficients  $c_{ja'}$  ( $c_{la}$ ). Furthermore we write  $\boldsymbol{\rho}_{C_l} = \tilde{e}_N \boldsymbol{\rho}_l + \sum_{j=1}^{N-1} \tilde{e}_j \mathbf{R}_j$ ,  $\boldsymbol{\rho}_k(\{\mathbf{R}\}) = \lambda_{k-1} \mathbf{R}_{k-1} - \sum_{j=k}^{N-1} \kappa_{j+1} \mathbf{R}_j$  and we use dressing of the initial wave function with factors  $\eta_d(\boldsymbol{\rho}_j, t) = \exp\{i \mathbf{k}_{\text{st}} \cdot \boldsymbol{\rho}_j\}$ ,  $\eta_u(\boldsymbol{\rho}_j, t) = \exp\{i [\mathbf{k}_{\text{st}} - \tilde{e}_N \mathbf{A}(t)] \cdot \boldsymbol{\rho}_j\}$ . The index  $l$  on  $\tilde{e}_j$  means that the charge distribution is such that the electron is ionized from (recombined with) the center  $l$ . For neutral polyatomic molecules we have  $\tilde{e}_N = -1$  and  $\boldsymbol{\rho}_{C_l} = \mathbf{0}$ ,  $l = 1, \dots, N$ , so that the expression for the time-dependent dipole simplifies.

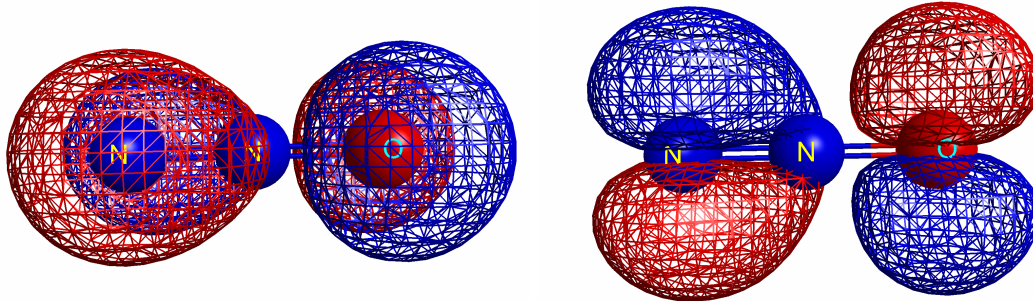
### 3. Numerical results

Now we are going to demonstrate the application of the presented theory using a simple example. We consider the HHG process of the nitrous oxide ( $\text{N}_2\text{O}$ ) molecule. Nitrous oxide, commonly known as laughing gas, is a colorless, odorless non-flammable gas. The  $\text{N}_2\text{O}$  molecule is a linear molecule with N-N (N-O) internuclear distances of 1.128Å(1.184Å) at the equilibrium geometry. Structure of the  $\text{N}_2\text{O}$  molecule belongs to the  $C_{\infty v}$  point group and its double degenerate HOMO, shown in Fig. 1, has the  $\pi$  symmetry. Vertical ionization energy of the  $\text{N}_2\text{O}$  molecule is  $I_p = 12.89$  eV.

Now, we present the calculated harmonic emission rate of the HHG process in a linearly polarized laser field, defined as  $\mathbf{E}(t) = E_0 \sin(\omega t) \hat{\mathbf{e}}_L$  and having the intensity  $4 \times 10^{14}$  W/cm<sup>2</sup> and the wavelength 800 nm. The molecule is oriented along  $z$  axis and  $\hat{\mathbf{e}}_L \equiv (\theta_L, \varphi_L)$  in spherical coordinates. We fix the laser field in the  $xz$  plane ( $\varphi_L = 0$ ) and change the polar angle  $\theta_L \in [0^\circ, 180^\circ]$ . In the upper panel of Fig. 2 we show in false colors the logarithm of the harmonic emission rate, Eq. (5), as a function of the angle  $\theta_L$  and the harmonic order  $n$ .

In the remaining panels we show the rates obtained using only the  $x$  (middle panel) and only the  $z$  (bottom panel) component of the  $T$ -matrix element, Eq. (6). One can see that the contributions of both components are comparable.

The HHG spectra exhibit a pronounced minimum for the angle  $\theta_L = 90^\circ$ . This minimum is caused by the nodal plane of the  $\text{N}_2\text{O}$  molecule. Furthermore, there are minima for the



**Figure 1.** Coordinate-space wave function for the HOMOs of  $N_2O$  molecule.

angles of  $\theta_L \approx 45^\circ$  and  $\theta_L \approx 135^\circ$ . These type of minima can be related to the interference of three contributions of the recombination matrix element, i.e. the interference of the recombining electronic wave packets. The three-point interference can be explained by the presented MSFA theory. It is possible to extract an interference factor [27] which becomes small for some specific values of  $n$ ,  $\theta_L$ , and  $\varphi_L$ .

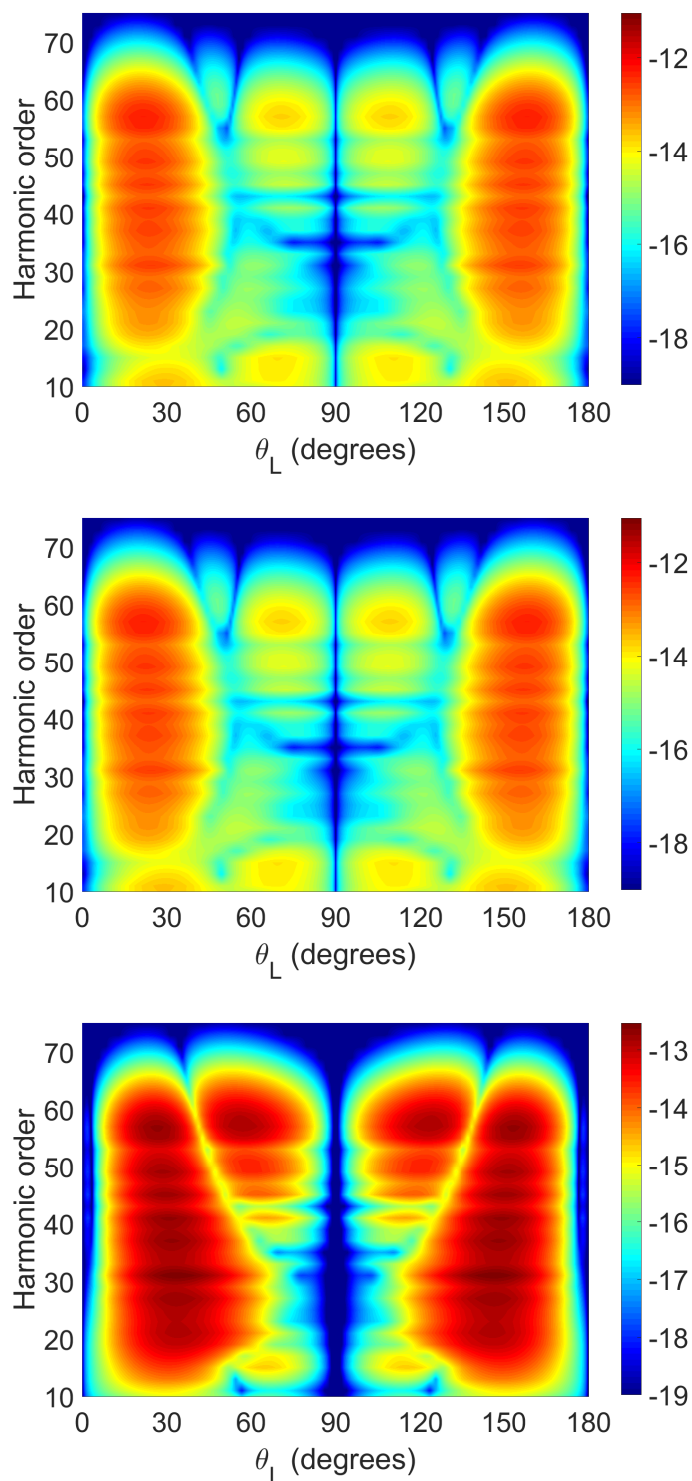
#### 4. Conclusions

We have used a strong-field-approximation-based theory of high-order harmonic generation by polyatomic molecules to calculate the harmonic emission rates of the nitrous oxide  $N_2O$  molecules. In our model, a polyatomic molecule is considered as a system of  $N + 1$  particles:  $N$  atomic (ionic) centers and one valence electron, emitted by strong-field ionization. In the Born-Oppenheimer and the fixed-nuclei approximation we derived an expression for the harmonic emission  $T$ -matrix element. Our theory is formulated in such a way that the strong-field approximation with the laser-field dressed or undressed initial and final states can be treated on the same footing.

We have shown that the harmonic emission rate of the ( $N_2O$ ) molecules exhibits minima for particular values of the orientation angle  $\theta_L$ . The appearance of these minima is related to the position of the nodal planes of the molecular HOMO as well as to the destructive interference of the recombining electronic wave packets. In general, for neutral polyatomic molecules the  $T$ -matrix element can be simplified and its recombination part can be extracted as a factor. This factor is responsible for a multicenter interference of the recombining electronic wave packets.

#### Acknowledgments

We gratefully acknowledge support by the Federal Ministry of Education and Science, Bosnia and Herzegovina.



**Figure 2.** Logarithm of the HHG rate of the  $\text{N}_2\text{O}$  molecule presented in false colors as a function of the orientation angle  $\theta_L$  and the harmonic order  $n$ . The results are obtained using both (top panel), only the  $x$  (middle panel), and only the  $z$  (bottom panel) component of the  $T$ -matrix element. Laser field is linearly polarized having the intensity  $4 \times 10^{14} \text{ W/cm}^2$  and the wavelength 800 nm. The initial state is dressed ( $q' = d$ ), while the final state is undressed ( $q = u$ ).

## References

- [1] Becker W, Grasbon F, Kopold F, Milošević D B, Paulus G G and Walther H 2002 *Adv. At. Mol. Opt. Phys.* **48** 35
- [2] Winterfeldt C, Spielmann C and Gerber G 2008 *Rev. Mod. Phys.* **80** 117
- [3] Agostini P and DiMauro L F 2004 *Rep. Prog. Phys.* **67** 813
- [4] Krausz F and Ivanov M 2009 *Rev. Mod. Phys.* **81** 163
- [5] Gaarde M B, Tate J L and Schafer K J 2008 *J. Phys. B* **41** 132001
- [6] Midorikawa K, Nabekawa Y and Suda A 2008 *Prog. Quant. Electron.* **32** 43
- [7] Pfeifer T, Abel M J, Nagel P M, Jullien A, Loh Z H, Bell M J, Neumark D M and Leone S R 2008 *Chem. Phys. Lett.* **463** 11
- [8] Corkum P B 1993 *Phys. Rev. Lett.* **71** 1994
- [9] Lein M, Hay N, Velotta R, Marangos J P and Knight P L 2002 *Phys. Rev. Lett.* **88** 183903
- [10] Itatani J, Levesque J, Zeidler D, Niikura H, Pepen H, Kiefer J C, Corkum P B and Villeneuve D M 2004 *Nature* **432** 867
- [11] Kopold R, Becker W and Kleber M 1998 *Phys. Rev. A* **58** 4022
- [12] Lein M, Hay N, Velotta R, Marangos J P and Knight P L 2002 *Phys. Rev. A* **66** 023805
- [13] Lagmago Kamta G and Bandrauk A D 2004 *Phys. Rev. A* **70** 011404(R)
- [14] Kanai T, Minemoto M and Sakai H 2005 *Nature* **435** 470
- [15] Vozzi C *et al* 2005 *Phys. Rev. Lett.* **95** 153902
- [16] Odžak S and Milošević D B 2009 *Phys. Rev. A* **79** 023414
- [17] Odžak S and Milošević D B 2009 *J. Phys. B* **42** 071001
- [18] Wagner N L, Wüest A, Christov I P, Popmintchev T, Zhou X, Murnane M M and Kapteyn H C 2006 *Proc. Natl Acad. Sci. USA* **103** 13279
- [19] Torres R *et al* 2007 *Phys. Rev. Lett.* **98** 203007
- [20] Li W, Zhou X, Lock R, Patchkovskii S, Stolow A, Kapteyn H C and Murnane M M 2008 *Science* **322** 1207
- [21] Wong M C H, Brichta J P and Bhardwaj V R 2010 *Phys. Rev. A* **81** 061402(R)
- [22] Wong M C H, Brichta J P, Spanner M, Patchkovskii S and Bhardwaj V R 2011 *Phys. Rev. A* **84** 051403
- [23] Wong M C H, Le A T, Alharbi A F, Boguslavskiy A E, Lucchese R R, Brichta J P, Lin C D and Bhardwaj V R 2013 *Phys. Rev. Lett.* **110** 033006
- [24] Le A T, Lucchese R R and Lin C D 2013 *Phys. Rev. A* **87** 063406
- [25] Ferré A *et al* 2015 *Nat. Commun.* **6** 6592
- [26] Kraus P M *et al* 2015 *Nat. Commun.* **6** 8039
- [27] Odžak S, Hasović E and Milošević D B 2016 *Phys. Rev. A* **93** 043413
- [28] Milošević D B and Ehloltzky F 2003 *Adv. At. Mol. Opt. Phys.* **49** 373