Odd-even harmonic generation from oriented CO and NO molecules within strong-field approximation

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Abstract.
Recently, the pure-even high-order harmonic generation (HHG) has theoretically found by the ab initio methods for CO molecules interacting with an intense laser. An examination of this phenomenon using the analytical approach such as the Lewenstein model, and for another polar molecular with other symmetry is needed. In this study, we theoretically investigate the odd-even harmonic generation from the CO and NO molecules in the linearly polarized laser field by using the Lewenstein model. Firstly, we confirm entirely the pure-odd and pure-even emission from CO whose molecular axis is perpendicular to the polarization direction of the laser. Secondly, we show that the odd-even behavior of the HHG spectra from NO is similar to that from the CO molecule. The HOMO’s symmetricity of the linear molecule does not change the odd-even property of the HHG spectra.

1. Introduction
High-order harmonic generation (HHG) is a highly nonlinear phenomenon when atoms or molecules interact with an intense ultrashort laser. The HHG offers a promising coherent sources to generate attosecond pulses [1, 2], and to probe the atomic or molecular structure [3–8].

There are two approaches to investigate the HHG theoretically. The first one is the ab initio methods such as numerically solving the time-dependent Schrödinger equation (TDSE) [3, 9], time-dependent density functional theory (TDDFT) [10], and multiconfiguration time-dependent Hartree-Fock (MCTDHF) [11] methods. The ab initio methods give the HHG spectra close to experimental data. However, they are too computational- and time-consuming even with a simplified single-active electron (SAE) approximation for many-electron atoms or molecules [12, 13]. The second approach is applying the analytical models such as Lewenstein model [14–16], quantitative rescattering (QRS) model [17]. These models have an advantage in saving computational time even for polyatomic molecules with good accuracy compared with the experimental data [15, 17]. The Lewenstein model utilizing the strong-field approximation (SFA) is a well-known semiclassical method to calculate HHG emission from atoms [14] and molecules [15, 16]. Accordingly, the HHG generation can be understood through the three steps
where electron (i) tunnels through the potential, (ii) quasi-classically moves in the laser field, and (iii) recombines to the parent ion.

Recently, a lot of effort has been focused on the polar (asymmetric) molecules [8,9,18–24] irradiated by a long-pulsed laser field. While atoms or symmetric molecules emit only odd harmonics [25–28], the asymmetric ones generate both odd and even orders [8,18–20]. Especially in 2017, Hu et al. [21] firstly found the pure-even harmonic generation from CO molecules in a linearly polarized laser field. Indeed, when the molecule axis of CO perpendicular to the laser polarization, the HHG with the polarization perpendicular to the electric field contains only even harmonics. This component of HHG is called the perpendicular HHG. On the contrary, the HHG emission, whose polarization is parallel to the polarization direction of the laser, covers only odd orders. This harmonic component is regarded as parallel HHG. A similar conclusion is also obtained by Heslar et al. [22] for CO in the bichromatic counter-rotating circularly polarized lasers. These interesting results [21, 22] were theoretically studied by applying the TDDFT method [10]. Moreover, the authors [21] claimed that the symmetry of the highest occupied molecular orbital (HOMO) is responsible for the generation of pure-even spectra. However, in their calculation, they adopted the multielectron method, including all orbitals. Therefore, recently, we exploited the TDSE method in the framework of SAE approximation to confirm the contribution of HOMO in pure-even harmonic generation from CO molecule [24]. In particular, in the TDSE method within SAE approximation, the electron wave packet is propagated from the HOMO only. So, by numerical calculation, we entirely proved that the HOMO’s symmetricity is the origin of this phenomenon [24]. Nevertheless, the TDSE is a time-consuming method, a confirmation by an analytical model dealing with the molecular HOMO such as Lewenstein models is still needed. On another hand, to obtain the clearer HHG peaks, i.e., odd and/or even HHG orders, one should use long-pulsed lasers. In this regime, as Ref. [29] figured out for hydrogen atom, we expect that the HHG calculations based on the dipole moments of molecules also meet the results from the acceleration dipoles as presented in previous studies [21–24]. Moreover, in mentioned-above studies, the investigation is performed for a molecular hydrogen ion with different nuclear charges [23], and CO molecules [21,22,24], whose HOMO has $\sigma$-type. The pure-even harmonic generation from a linear multielectron molecule with another symmetry, such as $\pi$-type is questionable.

In this study, we theoretically investigate the odd-even harmonic generation from the CO and NO molecules in the linearly polarized laser field by the Lewenstein model. Firstly, we confirm the pure-odd and pure-even HHGs from CO molecules. Besides, within SFA, we study of the transition between odd-even HHG to pure-odd or pure-even emission. Secondly, we examine the odd-even property of HHG spectra emitted from NO molecules whose HOMO, i.e., $\pi_{2p}$, is antibonding.

The organization of the paper is as follows. In Section 2, we describe some main points of the Lewenstein model for calculating HHG spectra. In Section 3, we present our results and discussion. Finally, we finish our paper with conclusions.

2. Computational method

In this study, the HHG spectra from perfectly pre-oriented CO and NO molecules are calculated in the framework of the strong-field approximation, i.e., using the Lewenstein model generalized to molecules, described in detail in Refs. [7,14–16]. We assume that the linear molecules are aligned along the $z$-axis, as shown in Fig. 1. The linearly polarized electric field $E(t)$ with the polarization lies in the $yz$-plane and makes an angle $\theta$ with the molecular axis called the orientation angle. Using the strong-field approximations, the time-dependent wave function of the Schrödinger equation can be expressed in the combinations of the ground and continuum states. Then, one can obtain the wave function in analytical form which is used for calculating the molecular dipole moment. After transforming to the laboratory frame, the component of
the induced dipole moment whose polarization is parallel to the electric field has the following form as in Ref. [7]

\[
D_{||}(t) = i \int_0^\infty d\tau \left( \frac{\pi}{\tau + \tau/2} \right)^{3/2} \left[ \cos \theta \, d_x^*(t) + \sin \theta \, d_y^*(t) \right] \times \left[ \cos \theta \, d_x(t-\tau) + \sin \theta \, d_y(t-\tau) \right] E(t-\tau) \times \exp[-iS_{st}(t,\tau)] a^*(t) a(t-\tau) + c.c. \tag{1}
\]

The perpendicular induced dipole moment has similar expression with \( \cos \theta \, d_z^*(t) + \sin \theta \, d_y^*(t) \) replaced by \( \sin \theta \, d_z^*(t) - \cos \theta \, d_y^*(t) \). Here, \( \varepsilon \) is a small positive constant; \( a(t) \) is the amplitude of the ground state; \( d(t) \equiv d[p_{st}(t,\tau) + \mathbf{A}(t)], d(t-\tau) \equiv d[p_{st}(t,\tau) + \mathbf{A}(t-\tau)] \) are the transition-dipole moment between the ground state and the continuum state, with \( p \) and \( \mathbf{A} \) are respectively the canonical momentum and vector potential of the laser field; and \( p_{st}(t,\tau) = - \int_{t-\tau}^t \mathbf{A}(t') dt' / \tau \) is the momentum at the stationary point of the action. The quasiclassical action at the stationary point is

\[
S_{st}(t,\tau) = \int_{t-\tau}^t \left( \frac{[p_{st}(t,\tau) - \mathbf{A}(t')]^2}{2} + I_p \right) dt', \tag{2}
\]

where \( I_p \) is the ionization potential.

\[\text{Figure 1. The HOMO of (a) CO molecule with } \sigma \text{ and (b) NO molecule with } \pi \text{ symmetry.}\]

The ground state of the molecule is attributed to its HOMO which can be obtained from the quantum chemical codes such as GAUSSIAN [30] or GAMESS [31]. In this study, the HOMO of CO and NO molecules is obtained by GAUSSIAN program applying Hartree-Fock (HF) method with aug-cc-pVTZ basis set. The HOMO of CO and NO are \( \sigma \) and \( \pi \) states (Fig. 1) with energy respectively equals 15.06 eV and 11.62 eV. Besides, the wave function of the continuum state is approximated by a plane wave \( |k\rangle \). In this paper, the depletion effect of the ground state is ignored. The HHG spectra with a fixed orientation angle can be calculated from the Fourier transform of the time-dependent induced dipole moment.

We use a laser with electric field \( E(t) = E_0 f(t) \sin(\omega_0 t) \), with peak amplitude \( E_0 \), carrier frequency \( \omega_0 \) and the sine-square envelope \( f(t) \). To obtain the HHG spectra with sharp peaks, a long-pulsed laser with 40 optical cycles, intensity of \( 1.5 \times 10^{14} \text{ W/cm}^2 \) and wavelength of 800 nm is used throughout this paper.
3. Results and discussion
In this section, firstly, we confirm the odd-even property of the HHG spectra from the CO molecule simulated by the Lewenstein model. Besides, we also discuss the odd-even HHG spectra when the orientation angle reaches 90°. Then, we expand the study to molecule NO whose HOMO (π-type) is an antibonding orbital.

3.1. Odd-even harmonic generation from CO molecule
Figure 2 presents the parallel and perpendicular HHG spectra emitted from the CO molecule calculated by the Lewenstein model for different orientation angles 0°, 45°, and 90°. It is shown that the HHG spectra have a typical shape that rapidly drops at some first harmonics, then follows by a flat plateau until the cutoff. The cutoff is about 28th order (Fig. 2) whose energy is consistent with the conventional cutoff law $I_p + 3.17U_p$ [14]. Moreover, the cutoff energy does not depend on the molecular orientation and the harmonic polarization. It is easy to understand since the cutoff energy only depends on the molecular ionization potential, and the kinetic energy of electron gained in the driving laser field.

![Figure 2](image)

**Figure 2.** The HHG spectra emitted from the CO molecule at orientation angles 0°, 45°, and 90°. For 0° and 45°, both odd and even harmonics appear in the HHG spectra. But at orientation angle 90°, the parallel HHG contains only odd orders, and only even harmonics exist in the perpendicular HHG.

Besides the shape of the spectra, we are interested in the odd-even property of HHG spectra. Note that the perpendicular component of the spectrum at 0° vanishes and only the parallel one exists. As shown in Fig. 2 for CO molecule, the HHG spectra at orientation angle 0° and 45° contain both odd and even harmonics. The similar behavior can be illustrated in both parallel and perpendicular HHG spectra for other orientation angles except 90° (Fig. 3). Especially, when the molecular axis is perpendicular to the electric field of the laser, i.e., at 90°, HHG spectra compose only odd harmonics for parallel (Fig. 2c) and, in contrast, only even order for perpendicular (Fig. 2d) polarizations. These results simulated by the Lewenstein model are similar to those obtained by the *ab initio* methods [21–24]. Also, we emphasize that the Lewenstein model deals with the molecular HOMO only, so the odd-even harmonic emission reflects the interaction of the linearly polarized laser field with the HOMO of the molecule. Therefore, the pure-even and pure-odd property of HHG spectra relates to the symmetry of the HOMO. In short, by the simple Lewenstein model, we confirm the pure-even and pure-odd harmonic generation from CO molecule when its axis perpendicular to the polarization direction of the electric field. Besides, the symmetry of HOMO is the origin of this phenomenon.
In recent work [24], we analytically explained the generation of pure-odd and pure-even at orientation angle 90° based on the Floquet theorem [25–28]. Indeed, only at 90°, i.e., when the electric field polarizes along the y-axis (Fig. 1a), the molecule-laser system is symmetric with the parity transformation \( P_2 : \ y \rightarrow -y, t \rightarrow t + T/2 \), where \( T \) is an optical-cycle duration. According to the Floquet theorem, we analytically proved that the parallel induced dipole moment is half-cycle ungerade while the perpendicular one is gerade [24]. As a consequence, its Fourier transform leads to the remaining of only odd harmonics in the parallel HHG, and only even orders in the perpendicular one [21, 24]. It is emphasized that at 90°, the perpendicular component of HHG vanishes for symmetric molecules, but exists for asymmetric one due to the possession of a permanent dipole [21]. For orientation angle different from 90°, the molecule-laser system does not satisfy the parity transformation \( P_2 \) or \( P : \{r \rightarrow -r, t \rightarrow t + T/2\} \). In turn, this symmetry-breaking leads to the appearance of both odd and even harmonics in HHG spectra [18–20, 24, 32, 33].

\[ \text{Figure 3. The HHG spectra emitted from CO molecule when orientation angles from 81° to 89°. With increasing the orientation angle, the intensity of even harmonics are gradually reduces for parallel HHG (left panels). On the contrary, the odd harmonics are suppressed when the orientation angle reaches 90° in perpendicular HHGs (right panels).} \]

Obviously, there is a transition between the odd-even emission to the pure-odd or pure-even HHG when the orientation angle reaches 90°. To clarify this point, in Fig. 3, we plot the parallel (left panels) and perpendicular (right panels) HHG spectra emitted from CO molecule for orientation angle from 81° to 89° calculated by the Lewenstein model. We can see in Fig. 3 that, with increasing of the orientation angle, in the parallel HHG, the even harmonics gradually lower and completely vanish at 90° (Fig. 2c). On the contrary, for the perpendicular HHG, the odd harmonics are suppressed, and only even orders remain at 90° (Fig. 2d). These effects are a consequence of the transition from the symmetry-breaking phase to the phase with symmetry \( P_2 \) [24] of the laser-molecule, more specifically, laser-HOMO system. These results are consistent with our obtained ones simulated by the TDSE method [24].

In summary, within the SFA, we confirm not only the pure-odd and pure-even harmonic generation from CO molecule at \( \theta = 90° \), but also the transition between two phases: odd-even HHG to pure-odd and pure-even HHG when the orientation angle reaches 90°. The Lewenstein model much saves the computational cost compared to the TDSE method. Besides, the Lewenstein model deals with the molecular HOMO only. As a consequence, the symmetricity of molecular HOMO relates to the odd-even behavior of HHG spectra.
3.2. Odd-even harmonic generation from NO molecule

Now we expand our study to another molecule NO, whose HOMO is $\pi$ antibonding symmetry. Figure 4 presents the HHG spectra emitted from NO molecule at orientation angles $0^\circ$, $45^\circ$ and $90^\circ$. We realize that the odd-even behavior of the HHG spectra from NO is identical to that from the CO molecule. In general, the HHG spectra of NO molecule contain both odd and even harmonics (Figs. 4a, b). But, at $90^\circ$, the HHG spectra are pure-odd for parallel (Fig. 4b), and pure-even for perpendicular (Fig. 4d) polarizations. We emphasize that although NO molecule possesses $\pi$ antibonding symmetry, its HOMO-laser system still satisfies the parity transformation $P_2$ when the molecular axis perpendicular to the electric field (see Fig. 1b). Therefore, the odd-even property for NO molecule does not change in comparison with that for CO.

![Figure 4](image)

**Figure 4.** The HHG spectra emitted from NO molecule at orientation angles $0^\circ$, $45^\circ$ and $90^\circ$. The behavior of the odd-even HHGs emitted from NO molecule is similar to that of CO as presented in Fig. 2.

4. Conclusion

By the Lewenstein model, we theoretically investigate the odd-even harmonic generation from the linear molecules, CO and NO, interacting with the long-pulsed linearly polarized intense laser pulse.

Firstly, we confirm the pure-odd and pure-even HHG spectra emitted from CO at orientation angle $90^\circ$, which are obtained by the *ab initio* methods in the previous studies. The calculation from the Lewenstein model indicates that the odd-even behavior of HHG spectra relates to the symmetricity of molecular HOMO only. Besides, the transition between the odd-even emission to the pure-odd or pure-even HHG when the orientation angle reaches $90^\circ$ is also examined. These results are consistent with the obtained ones by the TDSE method [24]. Secondly, we figure out that the odd-even behavior of the HHG spectra from NO is identical to that from the CO molecule. The HOMO’s symmetricity of the linear molecule does not change the odd-even property of the HHG spectra.

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