

Progress of selection rules in high-order harmonic generation

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Abstract. The high-order harmonic generation (HHG) has attracted much attention due to its wide application in attosecond science in last decades. The selection rules have also been broadly studied in experiments and theories since they play an important role in HHG. In this review, we give an overview of recent developments on selection rules of HHG from atoms to molecules. For targets with rotational symmetries, if the rotational symmetries of targets and laser pulses are the M -fold (the projective symmetry on the laser polarization plane) and L -fold, the selection rules are $Nk \pm 1$, where N is the the greatest common divisor of M and L . However, for asymmetric molecules in non-Born-Oppenheimer approximation, the situation is more complicated, where the nuclear dipole acceleration can produce even harmonics, but it is three orders lower than that of the electron. Hence, the HHG is mainly relied on the electronic dipole acceleration. In this case, the broken degree of system-symmetry dominates the generation of even-order harmonics.

1. Introduction

When atoms or molecules interact with strong laser fields, many interesting intense field phenomena will occur, such as high-order harmonic generation (HHG) [1-10], non-sequential double ionization [11], below-threshold harmonic generation (BTH) [12-16], multiple ionization [17,18], above-threshold ionization [19], and Coulomb explosion (CE) [20], and so on. These phenomena deepen on our understanding of dynamic mechanisms in the interaction between atoms or molecules and intense fields.

The HHG attracts a lot of attention since it provides a new type of coherence light source of ultra-short wavelength. Many fancy phenomena and applications have also been found in last decades [21-26]. One of the most important achievements is that the HHG supplies us an important avenue to generate ultra-short attosecond laser pulses [27, 28], which pushes the investigations on the ultra-fast measurement from the femtosecond magnitude to the attosecond magnitude [26].

The step of HHG developments dramatically increased in 1980s. Many groups successfully observed HHG from gaseous targets in experiments [29-34]. However, the early experiments only observed the harmonics with few orders. In 1993, Macklin *et al.* [33] firstly found that harmonics beyond 100 orders could be produced by a laser field with the wavelength of 806nm and the peak intensity $\geq 10^{15}$ W/cm². At the same year, L'Huillier *et al.* also reported the generation of 135th harmonics from Ne driven by a 1ps, 1.06 μ m laser pulse [34]. These findings indicate the potential possibility for the high efficient generation of coherent radiation at the extreme ultraviolet region (XUV).

After the HHG potential applications were discovered, the HHG has been widely investigated [35-37]. So far the physical

process of HHG can be well understood by the semi-classical three-step model [38]: ionization, acceleration and recombination. Moreover, the harmonic spectra produced from the atoms in a multi-cycle laser pulse present some common features: (i) the harmonic spectrum consists of three parts: a fast drop in the low-order yield, following a plateau and a sharp cutoff [39], the cutoff energy is around $I_p + 3.17U_p$, where I_p is the ionization energy of the atom and U_p is the ponderomotive energy [40], (ii) only odd harmonics are produced [41-43]. In order to explain the disappearance of even harmonics, the early explanation is given upon the foundation of a perturbative analysis about the non-linear optical susceptibilities [44]. However, since perturbation theory has been broken down in so strong fields, one may expect that a more reasonable explanation can be proposed. Then a non-perturbative proof which invokes the concept of inversion symmetry is given by Ben-Tal *et al.* [45]. In this theory, they concluded that when the system possesses inversion symmetry, the selection rules for HHG are $2k \pm 1$ ($k=1,2,3,\dots$), that is to say, the harmonic spectrum is composed of only odd harmonics.

Molecules have more degrees of freedom than that of atoms, thus the selection rules for the molecular high-order harmonic generation (MHOG) are more complex. Specifically, in a circularly polarized (CP) laser pulse, the allowed harmonics for molecular targets are determined by the rotational symmetries of molecules. If a molecule possesses M -fold rotational symmetry, the allowed harmonic orders in one CP laser field are $kM \pm 1$ (M is a positive integer and $k=0,1,2,\dots$), in which the efficiency of HHG is low [46]. In a linearly polarized (LP) laser field, the molecules with inversion symmetry obey the same selection rules as atoms [47]. Very recently, the group of professor Peixiang Lu [47] investigated the selection rules in HHG from more complicated molecules driven by different laser fields and got an important conclusion: the allowed harmonic orders can be directly judged by the associated rotational symmetries (ARS) of the target-laser system. For the stereoscopic targets, the ARS is determined by the symmetry of the projection of the targets rather than by the symmetry of the targets itself. For the laser pulse, the symmetry contributing to ARS can be decided by the symmetries of the Lissajous figure and its dynamical directivity [47]. Recently, the circularly polarized molecular high-order harmonics have been generated due to the

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optional selection rules of HHG in a bicircular laser [48, 49]. However, for asymmetric molecules in non-Born-Oppenheimer approximation, the situation is confusing. In 2001, Kreibich et al. firstly found that a model HD molecule can produce intense even harmonics in non-Born-Oppenheimer approximation [50]. Then the even harmonics were also observed from asymmetric molecules in Born-Oppenheimer approximation [51]. These works seemed to indicate that the even-order harmonics could appear as long as the systemic symmetry was broken regardless of in Born-Oppenheimer approximation or non-Born-Oppenheimer approximation. Nevertheless, in 2016, Du et al. found that the HD molecule still generated only odd harmonics in non-Born-Oppenheimer approximation though the generation of even harmonics is possible in principle [52]. Then Yue et al. investigated the HHG for HD^+ and HeH^{2+} in non-Born-Oppenheimer approximation and found that HD^+ generated only odd harmonics while HeH^{2+} generated both odd and even harmonics [53]. And they invoke a concept of broken degree of system-symmetry to interpret the different odd-even property between the harmonic spectra of asymmetric molecules HD^+ and HeH^{2+} [53].

The purpose of this review is to give an account of the history and recent status of the studies on the selection rules for HHG from atoms or molecules in Born-Oppenheimer approximation and non-Born-Oppenheimer approximation. The organization of this paper is as follows. In Sec. 2, we briefly introduce the methods of solving the time-dependent Schrödinger equation (TDSE). In Sec. 3, we will present the selection rules for HHG in Born-Oppenheimer approximation and non-Born-Oppenheimer approximation. Finally, we will summarize in Sec. 4.

2. Theoretical methods

In this section, we will sketch some theoretical methods for the HHG, including the numerical solution to TDSE in Born-Oppenheimer approximation and non-Born-Oppenheimer approximation.

2.1. Numerical solution of TDSE in Born-Oppenheimer approximation

Here we just present a one-dimensional (1D) numerical solution of TDSE using the split-operator method for the targets with two nuclei. For multiple-dimensional numerical solutions with different methods (e. g. B-spline). The readers can gain more details in relevant references and a recent review [54].

The 1D TDSE describing the interaction between targets and strong laser pulses in the dipole approximation and the length gauge can be given as (atomic units are used throughout)

$$i \frac{\partial}{\partial t} \Psi(x; t) = \left[-\frac{\partial^2}{2\partial x^2} + V(x) + E(t)x \right] \Psi(x, t), \quad (1)$$

with $V(x) = -Z_1/\sqrt{a + (x + R/2)^2} - Z_2/\sqrt{a + (x - R/2)^2}$, where Z_1 and Z_2 are the electric charges of two nuclei, and a is the soft-core parameter. R is the inter-nuclear distance. $E(t)$ is the laser field. In Born-Oppenheimer approximation, it assumes that the molecular vibrational period is longer than the laser pulse duration. Thus the nuclei are considered to be frozen. After the initial state is obtained by propagation in imaginary time. The equation (1) can be numerically solved by the split-operator method [55].

$$\Psi(x; t + \delta t) = e^{-iT\delta t/2} e^{-iV\delta t} e^{-iT\delta t/2} \Psi(x; t) + O(\delta t^3), \quad (2)$$

where T is the kinetic operator, and V is the interaction potential considering all the potential energy of systems. Then through the

Ehrenfest's theorem [56], the dipole acceleration $a(t)$ can be given as $a(t) = -\langle \Psi(t) | \nabla V | \Psi(t) \rangle$. Finally, one can obtain the harmonic spectrum by Fourier-transforming the dipole acceleration

$$S_q = \left| \int_{-\infty}^{+\infty} a(t) \exp(-iq\omega_0 t) dt \right|^2 \quad (3)$$

q is the harmonic order and ω_0 is the circular frequency of laser field.

2.2. Numerical solution of TDSE in non-Born-Oppenheimer approximation

To show the effect of the nuclear motion in the process of HHG, the numerical calculation of TDSE in non-Born-Oppenheimer approximation is proposed [50]. In this part, we only introduce a numerical calculation for a typical HD molecule with two electrons and two nuclei. In this calculation, the interaction between the HD molecule and the laser field is treated within dipole approximation. Then the Hamiltonian reads

$$H = -\frac{1}{2\mu_n} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e} \left(\frac{\partial^2}{\partial z_1^2} + \frac{\partial^2}{\partial z_2^2} \right) + \frac{1}{R} + w(z_1, z_2) - \sum_{j=1}^2 w(z_j, \frac{M_2}{Mn} R) - \sum_{j=1}^2 w(z_j, \frac{M_1}{Mn} R) + E(t) \hat{D} \quad (4)$$

with the dipole operator $\hat{D} = -(z_1 + z_2) - \lambda R$. For the interactions, it chooses the soft Coulomb potential [57]

$$w(x, y) = \frac{1}{\sqrt{(x-y)^2 + 1}} \quad (5)$$

z_1 and z_2 are the coordinates of two electrons. R is the inter-nuclear distance, and $Mn = M_1 + M_2$ is the total nuclear mass. $\mu_e = M_n/(M_n + 1)$ and $\mu_n = M_1 M_2 / M_n$ are respectively the reduced mass of nucleus and electron. $E(t)$ is the laser field, and $\lambda = (M_2 - M_1)/M_n$ is the mass-asymmetry parameter. The time-dependent wave function can be obtained by numerical solving TDSE using the Crank-Nicolson method [58]. Then the dipole moment can be got by

$$d(t) = \langle \psi(t) | \hat{D} | \psi(t) \rangle = -\langle \psi(t) | z_1 + z_2 | \psi(t) \rangle - \lambda \langle \psi(t) | R | \psi(t) \rangle = d_e(t) + \lambda d_n(t) \quad (6)$$

$d_e(t)$ and $d_n(t)$ are the electronic dipole moment and the relative nuclear dipole moment, respectively. The corresponding dipole acceleration is given via Ehrenfest's theorem [56]

$$a(t) = -\frac{1}{\mu_e} \langle \psi(t) | \frac{\partial H}{\partial z_1} + \frac{\partial H}{\partial z_2} | \psi(t) \rangle - \frac{\lambda}{\mu_n} \langle \psi(t) | \frac{\partial H}{\partial R} | \psi(t) \rangle = a_e(t) + \lambda a_n(t) \quad (7)$$

where $a_e(t)$ and $a_n(t)$ are the electronic dipole acceleration and the relative nuclear dipole acceleration. The harmonic spectrum can be easily got by Fourier-transforming the dipole acceleration.

For the numerical calculation of TDSE for molecular ion, it is similar to that of HD molecule. The relative details can be found in Refs. [50, 53, 59].

3. The selection rules for HHG from atoms and molecules in Born-Oppenheimer approximation and non-Born-Oppenheimer approximation

After the HHG being a hot topic, the selection rules as an important feature of HHG attract much attention. We will start from investigations of the selection rule for atomic HHG, including the early experimental results and the theoretical studies. Then we will review the selection rules of HHG from molecules possessing symmetry to asymmetric molecules in Born-

Oppenheimer approximation and non-Born-Oppenheimer approximation. It aims to give a detailed knowledge of selection rules for MHOHG in recent researches in non-Born-Oppenheimer approximation.

3.1. The selection rules for HHG from atoms

In 1988, the suppression of even harmonics in the harmonic generation spectra (HGS) from Xe has been observed in experiment [41]. In the following, X. F. Li et al. presented an experimental measurement of HHG in a 15-Torr rare-gas medium exposed to a strong 1064-nm laser field [42]. They also noticed the vanish of even harmonics in HGS for different rare gases. Their experimental results are reproduced in figure 1, which shows that the HGS are composed of only odd harmonics for different rare gases. Aroused by the experimental studies, there were some theoretical works for HHG [50-62]. And the conclusion of the theoretical simulation is in good agreement with that of the experiments [42]. As one can see from the theoretical results in figure 2, there is only odd harmonics in the HGS for Xe. The corresponding explanation is based on the non-linear optics, which employs a perturbative analysis [44]. But, as well known, the perturbative theory is inapplicable to the strong fields. Thus it is urgent to find a non-perturbative theoretical interpretation.

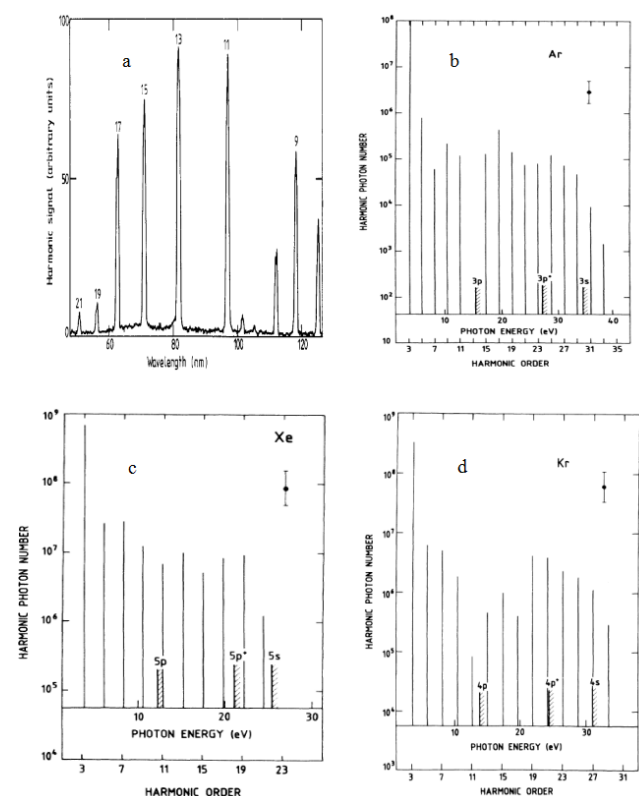


Figure 1: (a) Harmonic spectrum obtained using Xe gas. The laser intensity was about $3 \times 10^{13} \text{ W/cm}^2$ and the Xe pressure was approximately 10 Torr. The harmonic spectra obtained from (b) Ar, (c) Xe and (d) Kr by a laser field with the peak intensity of $3 \times 10^{13} \text{ W/cm}^2$ and the wavelength of 1064nm. The gaseous pressure was 15 Torr. (a) is taken from [41], (b), (c) and (d) are taken from [42].

Then in 1993, Ben-tal et al. proposed an alternative proof which does not use perturbation theory and therefore holds for the strong fields [45]. The proof can be reproduced in the following: The probability to gain n th harmonic from a system is given

$$\sigma_{\epsilon}^{(n)} \propto n^4 \left| \langle \phi_{\epsilon}(\vec{r}, t) | \hat{D} e^{-in\omega_0 t} | \phi_{\epsilon}(\vec{r}, t) \rangle \right|^2 \quad (8)$$

where $\phi_{\epsilon}(\vec{r}, t)$ is given by $\Psi_{\epsilon}(\vec{r}, t) = \exp(-i\epsilon t) \phi_{\epsilon}(\vec{r}, t)$. The $\phi_{\epsilon}(\vec{r}, t)$ is the single Floquet state. ϵ is named quasi-energy. The double bracket notation stands for the integral over space and time. \hat{D} and ω_0 are the dipole moment operator and the laser circular frequency, respectively. For atomic system with a LP laser field, the Hamiltonian $H(t)$ is invariant under the second dynamics symmetry (DS) operator

$$\hat{P}_2 = (r \rightarrow -r, t \rightarrow t + \pi/\omega_0), \quad (9)$$

The n th harmonic is therefore emitted only if

$$\begin{aligned} & \ll \phi_{\epsilon}(\vec{r}, t) | \hat{D} e^{-in\omega_0 t} | \phi_{\epsilon}(\vec{r}, t) \gg \\ & = \ll \hat{P}_2 \phi_{\epsilon}(\vec{r}, t) | \hat{P}_2 \hat{D} e^{-in\omega_0 t} \hat{P}_2^{-1} | \phi_{\epsilon}(\vec{r}, t) \gg \\ & \neq 0, \end{aligned} \quad (10)$$

which leads to

$$\hat{D}(\vec{r}) \exp[-in\omega_0 t] = \hat{D}(-\vec{r}) \exp[-in\omega_0(t + \pi/\omega_0)], \quad (11)$$

This indicates that the allowed harmonics are odd orders (n is odd). And the theoretical explanation holds for HGS of any symmetric atomic system. Actually, one also noticed that the systemic symmetry depended on both the symmetry of the atoms and laser fields. In 1995, S. Long et al. found that the allowed harmonic orders were only relied on the symmetry of laser pulses for atomic targets, because the atoms are spherical symmetry [63].

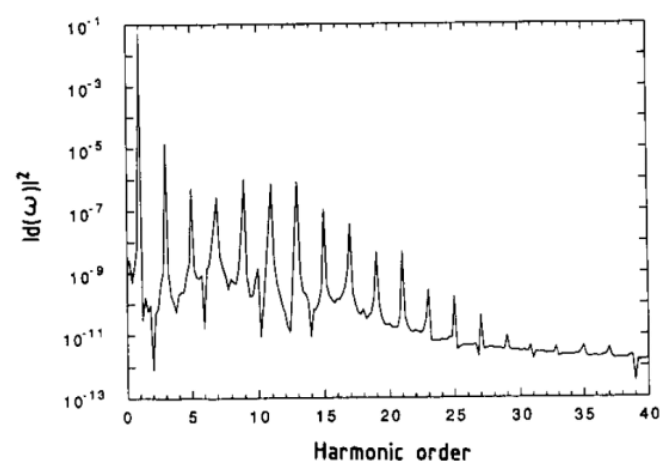


Figure 2: The harmonic spectrum for Xe by a 1064-nm laser pulse with the peak intensity of $3 \times 10^{13} \text{ W/cm}^2$, obtained from the theoretical calculation. Reprinted figure from [62].

3.2. The selection rules for HHG of molecules with rotational symmetries in Born-Oppenheimer approximation.

Molecules have more degrees of freedom than atoms which is the reason that the HGS exhibit rich properties, thus the selection rules of MHOHG are more complex. In 1998, O. E. Alon et al. discussed the application of the dynamical symmetry of crystals to generate high harmonics [46]. In their theory, for symmetric targets in CP laser field, the Hamiltonian keeps invariant under a N -fold transformation,

$$\hat{P}_N = (\varphi \rightarrow \varphi + 2\pi/N, t \rightarrow t + 2\pi/N\omega_0), \quad (12)$$

where t is the time and φ is the azimuth angle. Therefore the nonzero term of $\sigma_{\epsilon}^{(n)}$ equation (8) meets:

$$\exp[-i \frac{2\pi(n \pm 1)}{N}] = 1, \quad (13)$$

It is fulfilled only with $n = kN \pm 1$, where k is an integer. They presented the HGS of accurate numerical calculations for $N=100$, which was

reprinted in figure 3. As expected, the generation of harmonics were the 99th, 101th, 199th, 201th, ... Orders. Their work extends the selection rules of atomic HHG to the systems with N -fold rotational symmetry. In other words, for a molecule possessing N -fold rotational symmetry, the allowed harmonics in CP laser field are $n=kN\pm 1$ (N is a positive integer and $k=0,1,2,\dots$) [46]. For the molecules with inversion symmetry ($N=2$), they obey the same selection rules as atoms in LP laser pulses.

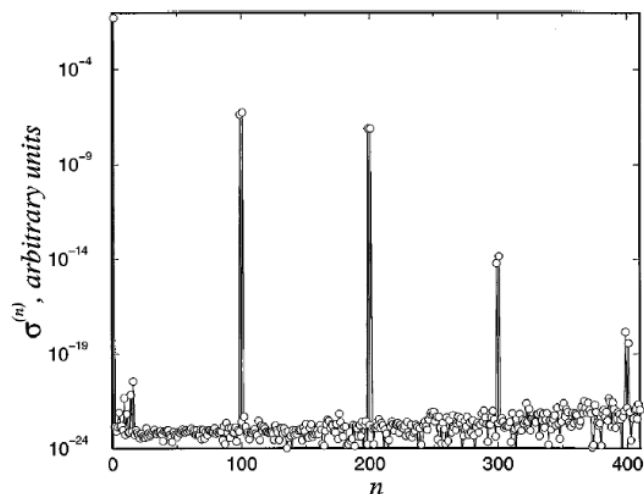


Figure 3: The harmonic spectrum for models of $N=100$, which is placed equidistantly on a circle in a CP laser field with the intensity of $1.8\times 10^{13}\text{W}/\text{cm}^2$. Reprinted figure from [46].

Very recently, X. Liu et al. demonstrated the selection rules based on the associated rotational symmetry (ARS) of the target-laser system [47]. Firstly, they studied the selection rules for planar-molecular HHG in different laser fields. They defined that if a molecule possessed M -fold rotational symmetry, it denoted as CM. Similar to targets, the L -fold symmetries of laser fields are expressed as CL. Their results are shown in figure 4. The Lissajous figures of the CP, LP, (1:2 and 1:3) counter-rotating bicircular (CRB) laser fields are shown in the top row of the Figs. 4, respectively. The HGS of BCl₃ and C₆H₆ molecules by CP, LP, 1:2CRB and 1:3CRB laser fields are exhibited in figures (a)-(h). In Figs.(a) and (e), the selection rules are respective $3k\pm 1$ and $6k\pm 1$, which correspond to the truth that the BCl₃ and C₆H₆ molecules possess

C3 and C6 symmetry. It indicates that the allowed harmonics driven by CP laser fields are only relied on the symmetries of the molecules ($n=kN\pm 1$), which agrees well with the conclusion in Ref. [46].

In fact, the allowed harmonics are determined by the greatest common divisor (GCD) of ARS for the molecules and laser fields, which is demonstrated by F. Mauger et al. [64]. In this theory, the DS operator $\hat{P}_{\tilde{N}}$ should be substituted by the operator $\hat{P}_{\tilde{N}}$, where \tilde{N} is the GCD of the ARS for the molecules and laser fields. In conclusion, the selection rules are $k\tilde{N}\pm 1$ when the full time-dependent Hamiltonian is invariant under a combined \tilde{N} -fold transformation. Then in figure 4(b), the BCl₃ and LP laser field have C3 ($M=3$) and C2 ($L=2$) symmetry, respectively. Because the GCD of M and L is 1, the allowed harmonics are $k\pm 1$. In figure 4(g), C₆H₆ and 1:2CRB laser field possess C6 ($M=6$) and C3 ($L=3$) symmetry. The GCD of M and L is 3. Corresponding, the selection rules of HGS are $3k\pm 1$. The results of figures 4 (c), (d), (f) and (h) are also explained based on the GCD rule of symmetries in the paper [47]. Here, we do not repeat again.

The above results show that the selection rules for planar molecules are dependent on the ARS of the molecules and laser fields: If the molecules and laser fields possess M -fold and L -fold symmetries, the allowed harmonics should be $Nk\pm 1$ orders, in which N is the GCD of M and L .

Next, they further investigated the selection rules for stereoscopic molecules. They discovered that the effective symmetry of the stereoscopic molecule should rely on the rotational symmetry of its projection on the polarization plane, rather than that of the target itself. They showed the HGS for different oriented SF₆, in which the laser pulses were along the z -axis. The results are shown in figure 5. For SF₆ orientated as Fig. 5(a), the projection on the polarization plane (x - y) is a regular hexagon with C6 symmetry. Thus the GCDs of ARS in 1:2(C3), 1:3(C4), 1:5(C6) CRB laser fields are C3, C2, and C6, and the selection rules should be $3k\pm 1$, $2k\pm 1$, and $6k\pm 1$, which agrees with the results in Figs. 5(b)-5(d). For SF₆ orientated as Fig. 5(e), the projection on the polarization x - y plane forms a square with C4 symmetry. The corresponding GCDs of ARS are 1, 4, and 2. Therefore, the harmonics obey $k\pm 1$, $4k\pm 1$, and $2k\pm 1$ selection rules. The HGS are shown in Figs. 5(f)-5(h).

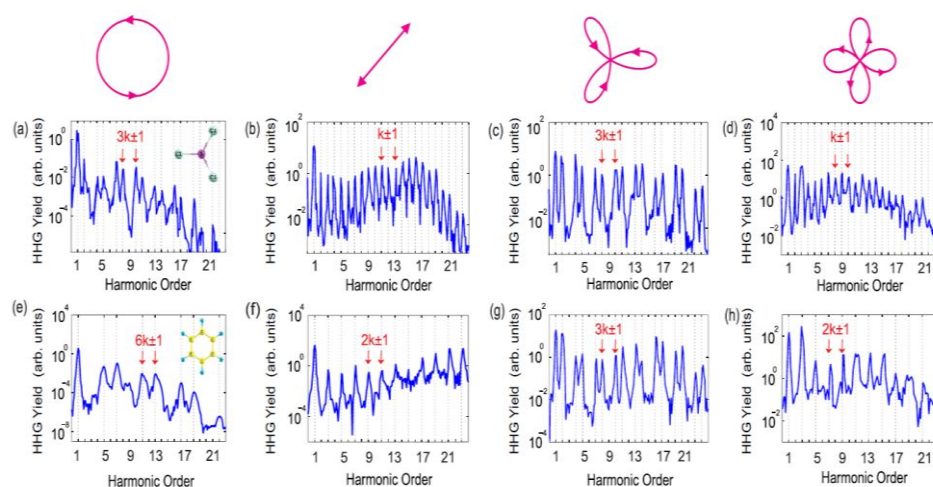


Figure 4: The harmonic spectra from (a)-(d) BCl₃ and (e)-(h) C₆H₆ driven by LP, CP, 1:2CRB, 1:3CRB laser fields. The top row shows the Lissajous figures of laser fields. Reprinted figure from [47].

In addition, they also found that the symmetry of a laser field could not be intuitively judged only by the geometric structure (that is to say, the selection rules also depended on the dynamical directivity of the laser fields). They displayed that when considered the dynamical directivity of laser fields, the orthogonal two-color (OTC) laser fields with frequency ratios 1:2 and 1:3 respectively had C_1 and C_2 symmetries instead of both C_2 symmetry. In order to confirm the above conclusion, the authors calculated the HGS from CO and N_2 driven by 1:2 and 1:3OTC laser pulses, as shown in Fig. 6. One can see that the allowed harmonic

orders are both $k\pm 1$ in figures 6(a) and 6(b). This is because that the CO possesses C_1 symmetry, which leads to the ARS always being C_1 regardless of fields. For figure 6(c), the allowed harmonics are $k\pm 1$, because the ARS of N_2 (C_2 symmetry) and 1:2OTC field (C_1 symmetry) is C_1 . For figure 6(d), the allowed harmonics are $2k\pm 1$, because the symmetries of N_2 and 1:3OTC field are both C_2 (the ARS is C_2). As for their previous calculations using LP, CP and CRB laser fields, the symmetries do not change when dynamical directivity of the laser pulses are taken into account.

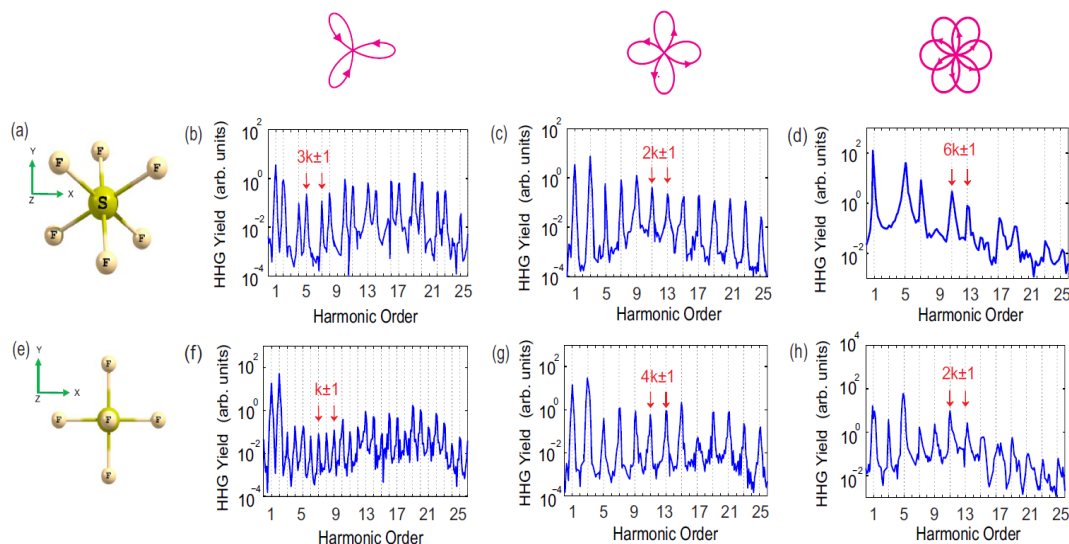


Figure 5: The top views of two different oriented SF6 molecules from the z-axis are shown in (a) and (e). The harmonic spectra from SF6 orientated as in Fig. 5(a) by (b)1:2, (c)1:3, and (d)1:5 CRB laser fields, and the laser pulses are along the z-axis. (f)-(h) same as (b)-(d), but for SF6 orientated as in Fig. 5(e). Reprinted figure from [47].

Their work shows that the ARS contributes to the selection rules for MHOHG: For the stereoscopic molecules, the ARS dominates by the symmetry of the projection of the molecule rather than by the symmetry of the molecule itself. For the laser field, the ARS could be judged by the symmetries of the Lissajous figure and its dynamical directivity. And the ARS of molecules and laser fields obeys the GCD rule. For the molecules and laser fields with M -fold and L -fold symmetries, the selection rules are $Nk\pm 1$, in which the GCD of M and L is N . This theory can also apply to atoms (the symmetry of $M = \infty$).

3.3. The selection rules for HHG from asymmetric molecules in non-Born-Oppenheimer approximation.

In fact, Ben-Tal *et al.* had already pointed out that even harmonics might appear when the systemic symmetry was broken by modifying the laser field and potential in the end of their paper [45]. But, the truth tells us that there is a more complex physics process for asymmetric molecules in non-Born-Oppenheimer approximation.

In 2001, M. Lein *et al.* first investigated the harmonic generation from HD and H_2 molecules beyond Born-Oppenheimer approximation [50]. They found that for H_2 , the HGS only exhibit odd orders (Fig. 7(b)), while for HD, the even harmonics were also observed (Fig. 7(a)). They attributed it to the influence of non-Born-Oppenheimer approximation. In the non-Born-Oppenheimer approximation, the asymmetry parameter λ of H_2 is equal to 0, thus it obeys the same selection rules as molecules with inversion symmetry ($2k\pm 1$). Whereas, for HD, due to $\lambda \neq 0$, the symmetry of HD molecule is broken and the even harmonics thus can appear in principle.

A few years later, in a theoretical work about attosecond pulses from an asymmetric molecule [51], both the odd and even harmonics were observed from the asymmetric molecule in Born-Oppenheimer approximation. The theoretical calculation is shown in Fig. 8. One can find that for an asymmetric molecule, the HGS are composed of odd and even harmonic orders, but for an atom only odd harmonics in figure 8. Their theoretical explanation shows that when asymmetric molecules interact with laser pulses, the ionization is asymmetry, which leads to the generation of even harmonics.

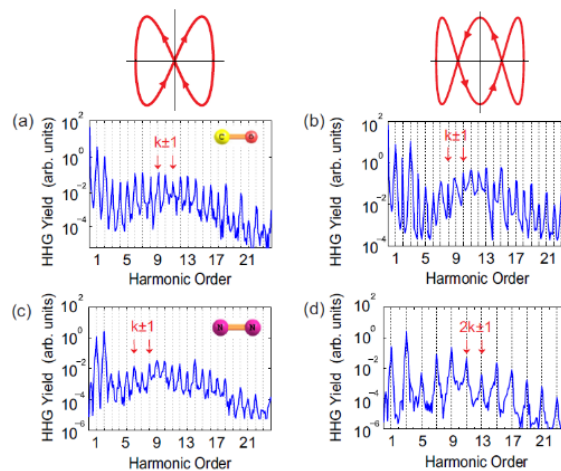


Figure 6: The harmonic spectra from CO obtained by (a)1:2 and (b) 1:3OTC laser pulses. (c) and (d) same as (a) and (b) but for N_2 . The Lissajous figures of laser fields are shown on the top row. Reprinted figure from [47].

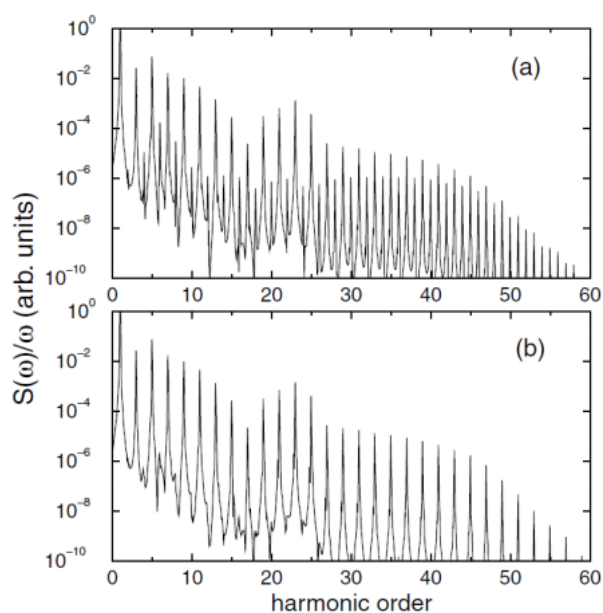


Figure 7: The harmonic spectra obtained from (a) HD and (b) H₂ molecules in non-Born-Oppenheimer approximation. The laser pulse is 770nm with a peak intensity of 10¹⁴W/cm². Taken from [50].

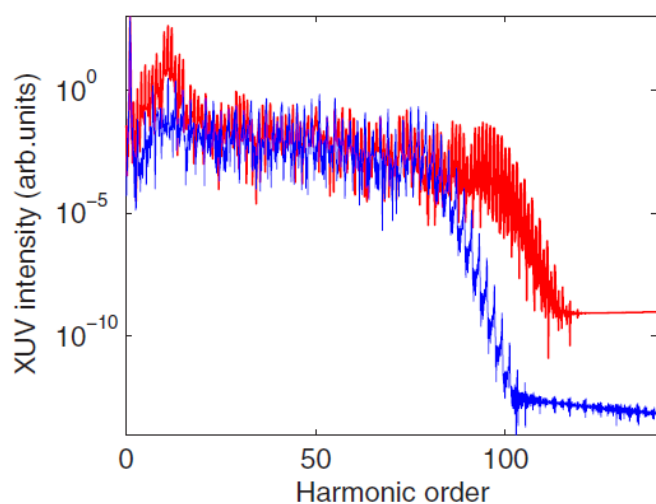


Figure 8: Spectra of harmonics from the atom (blue line) and the asymmetric molecule (red line) driven by a 800nm laser pulse. The peak intensity of the laser pulse is 5×10¹⁴W/cm². Taken from [51].

The above two works seem to indicate a fact that if the symmetry of molecules is broken, the even harmonics should be produced regardless of in Born-Oppenheimer approximation or non-Born-Oppenheimer approximation. Unluckily, in 2016, Du *et al.* restudied the HHG from HD molecule in non-Born-Oppenheimer approximation [52]. An unexpected result occurs, which is that HD only produces odd harmonics, as shown in Fig. 9(a). Their further analysis reveals that though the nuclear dipole moment can contribute to the generation of even harmonics, there are still only odd harmonics in the HGS of HD, because the nuclear acceleration is three orders of magnitude lower than the electronic acceleration. The result is reproduced in Fig. 10. It is clear that the nuclear dipole acceleration can make contribution to the generation of even harmonics (Fig. 10(a)), but the acceleration of electron is about three orders of magnitude larger than that of nuclei (Fig. 10(b)). One also finds that the contribution of nuclear acceleration to the HGS can be ignored in Fig. 9(a), in which the HGS calculated with

$a_e(t) + \lambda a_n(t)$ are same as that calculated with $a_e(t)$.

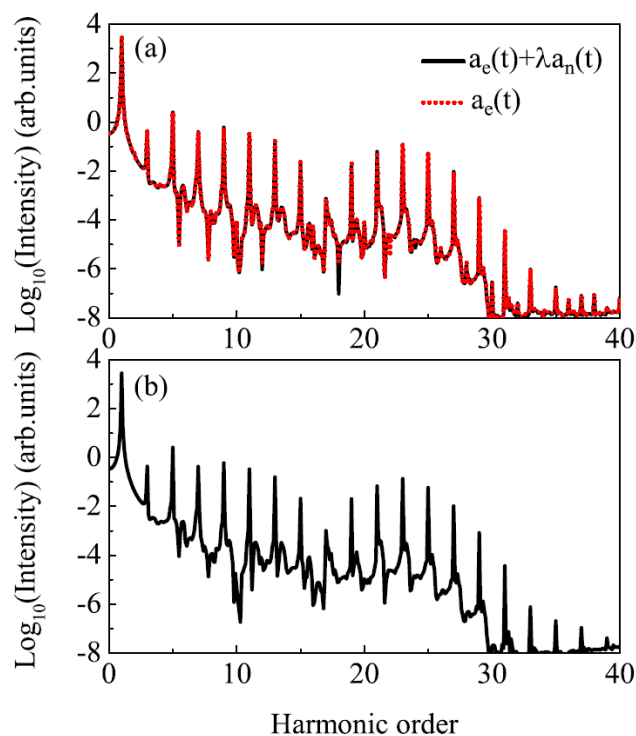


Figure 9: (a) The harmonic spectrum calculated with (black solid line) $a_e(t) + \lambda a_n(t)$ and (red dotted line) $a_e(t)$ for HD molecule. (b) The harmonic spectrum for H₂ molecule. Reprinted figure from [52].

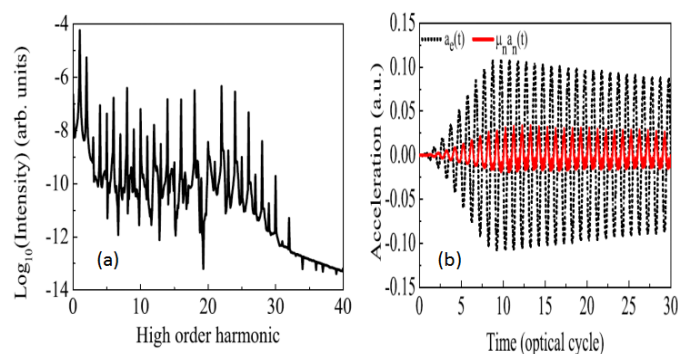


Figure 10: (a) The harmonic spectrum for HD molecule calculated with the nuclear dipole acceleration $a_n(t)$. (b) The corresponding acceleration of (black dotted line) electron and (red solid line) nuclei. The nuclear acceleration is amplified by $\mu_n(M_1M_2/M_n)$ times. Reprinted figure from [52].

The next year, Yue *et al.* did a research on the HHG for asymmetry molecules of HD⁺ and HeH²⁺ in non-Born-Oppenheimer approximation. They found that HD⁺ produced only odd harmonic (Fig. 11(b)), but HeH²⁺ produced both odd and even harmonic (Fig. 11(c)). This finding confirms the conclusion that the electronic acceleration dominates the HHG in Ref. [52]. However, it cannot explain that the different odd-even property of the HGS for HD⁺ and HeH²⁺. Then through comparing the Coulomb potential of H₂⁺, HD⁺ and HeH²⁺, they found that the potential well of H₂⁺ and HD⁺ is symmetry, though the potential well of HD⁺ has a few translation due to the mass-asymmetry. While for HeH²⁺, the mass and electron are both asymmetric, hence the potential well is dramatically broken. We can get the above messages from figure. 12. Thus a concept of the broken degree of systems is invoked to explicate the difference of the odd-even property in the HGS

between HD^+ and HeH^{2+} . Specifically, for HD^+ the systemic symmetry is broken in a tiny degree, which owes to the effect of nuclear acceleration. But this effect can be ignored. Hence, only odd harmonics appear in the HGS. For HeH^{2+} , both odd and even harmonics are obtained due to the acute broken degree of the system.

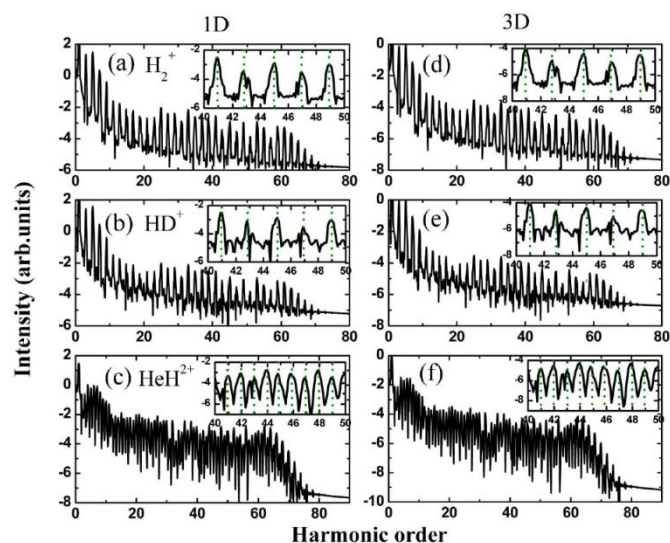


Figure 11: The harmonic spectra from (a) H_2^+ , (b) HD^+ and (c) HeH^{2+} by a 770nm laser pulse with the intensity of $4 \times 10^{14} \text{W/cm}^2$. The insets are the enlarged area of the HGS from 40 to 50. The left (right) column is the 1D (3D) simulations. Reprinted figure from [53].

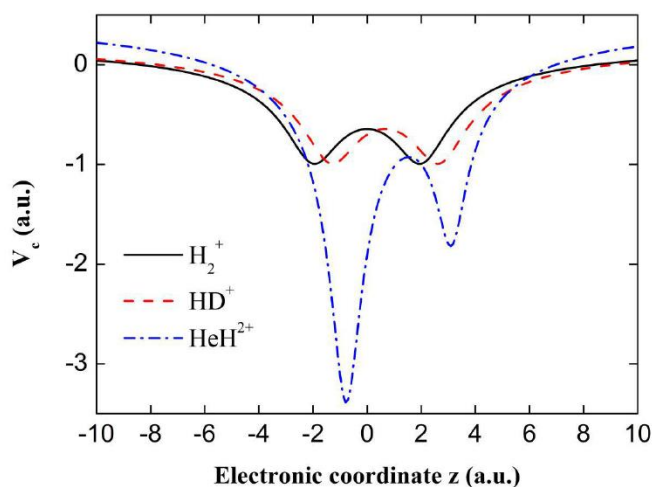


Figure 12: Coulomb potential for (black solid line) H_2^+ , (red dashed line) HD^+ and (blue dashed-dotted line) HeH^{2+} . Reprinted figure from [53].

4. Conclusions

The harmonic spectra obtained from the interaction between strong laser pulses and targets can be applied to creating coherent light sources and ultra-fast detection. In order to well understand the progresses of HHG, one needs to grasp some important features of HHG, in which one of these characters is the generation of odd-even order harmonics. The recent studies reveal that the selection rules of HHG for different targets are quite intricate in non-Born-Oppenheimer approximation.

For rotational-symmetric targets, the ARS of targets and laser pulses dominates the HHG. And the ARS follows the GCD rules. In detail, when the targets and laser pulses possess M -fold (the

effective symmetry, which is the projection-symmetry on the polarization plane) and L -fold rotational symmetries, the selection rules of HHG ought to be $Nk \pm 1$, where N is the GCD of M and L .

For asymmetry targets in non-Born-Oppenheimer approximation, the allowed harmonic orders in the HGS are relied on the electronic dipole acceleration, since the electronic dipole acceleration is three orders of magnitude larger than that of nuclei, though the nuclear dipole acceleration can contribute to generating even harmonics. Moreover, both odd and even harmonics may be produced when the symmetry of systems is broken. However, the obvious even harmonics can be obtained only if the systemic symmetry is broken to a certain degree.

However, it is still an open question how to define the broken degree of the systemic symmetry, which needs us to further investigate. In addition, when targets interact with the CRB laser pulse, the influence of the ionization symmetry to selection rules of HHG will be a significant topic to be addressed in the future.

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