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Highly efficient high-order harmonic generation by metallic carbon nanotubes

G. Ya. Slepyan,[1] S. A. Maksimenko,[1] V. P. Kalosha,[1,2] J. Herrmann,[2] E. E. B. Campbell,[3] and I. V. Hertel[2]
[1]*Institute for Nuclear Problems, Belarus State University, Bobruiskaya 11, 220050 Minsk, Belarus*
[2]*Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Straße 2a, D-12489 Berlin, Germany*
[3]*Göteborg University and Chalmers University of Technology, S-41296, Göteborg, Sweden*
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High-order harmonic generation by metallic carbon nanotubes exposed to an intense ultrashort pulse has been theoretically investigated in the semiclassical approximation. The mechanism of nonlinearity provided by the motion of conduction electrons below the band of optical resonances has been considered. It has been shown that the high density of states of conduction electrons in metallic carbon nanotubes and the specific dispersion law inherent in hexagonal crystalline structure as well as the transverse quantization of the electron momentum result in a uniquely high efficiency of the current conversion to high-order harmonics. [S1050-2947(99)50708-7]

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The discovery by Iijima [1] of quasi-one-dimensional crystalline carbon nanotubes (CNs) has attracted much attention to their mechanical and electronic properties [2]. Peculiar transport and optical properties of CNs arise from the varied kinds of geometrical and chiral symmetry as well as from the nanoscale size. In particular, owing to the quasi-one-dimensional topology of CNs they can manifest either metallic or semiconducting properties, depending on the radius and chiral angle. One can expect especially broad potentialities for the manifestation of such peculiarities on exposing CNs to strong electromagnetic fields, which provide a nonlinear interaction. The role of nonlinearity in the electron transport has been considered in Refs. [3,4], where a nonlinear mechanism of the chiral current formation that is unique for CNs has been revealed. The third-order nonlinear optical susceptibility of CNs has been evaluated in Refs. [5,6]. It has been shown that the susceptibility spectrum displays a pronounced resonance, with the line intensity significantly exceeding the line intensities in other nonlinear materials.

The strong nonlinearity of CNs is determined by the fact that the electron motion is governed by a strongly nonparabolic dispersion law. This peculiarity of nanotubes raises the question of whether these structures can be used for high-order harmonic generation (HHG). There is currently great interest in the production of extreme-ultraviolet and soft-x-ray radiation by HHG. The majority of this work has concentrated on generating harmonics from the interaction of intense subpicosecond laser pulses with gaseous targets [7–9]. The coherent high-order odd harmonics are produced in the strong-field regime due to tunneling of electrons to the continuum and their return to the atomic core under the action of the oscillating field. The high-order harmonic spectrum has a very characteristic shape: it falls off for the first few harmonics, then exhibits a plateau where all the harmonics have approximately the same strength, and ends up with a sharp cutoff. Much progress has been achieved using this approach, and coherent radiation with photon energies up to 0.5 KeV has been produced [10,11]. A second mechanism of the HHG is the interaction of intense laser pulses with solid targets [12,13]. In this case, the electrons oscillate at close to relativistic velocities across the solid-vacuum boundary or the sharp plasma-vacuum interface. The dramatic electron-density gradient in a distance much less than the wavelength of light forms an oscillating mirror [14,15], giving rise to radiation of odd and even harmonics.

In the present paper, we study an alternative to the above-described approaches: optical high-order harmonic generation by conduction electrons confined at the cylindrical surface of a metallic CN illuminated by an intense field. Conduction electrons with energies below the energy of the interband transitions move in the crystalline field like free quasiparticles, with a modified dispersion law allowing us to apply a quasiclassical approach to describe the electron motion. The high density of states for such electrons is characteristic for metallic CNs. At least three reasons can be given why the HHG by CNs is of interest. First, the pronounced electron nonlinearity in CNs with the two-dimensional (2D) confined electron distribution on the surface shows some potential for the generation of high-order harmonics and could thus represent a useful mechanism for the generation of coherent ultrashort light pulses at very short wavelengths. Second, the method considered here allows the generation of radiation with very short wavelengths in a device confined to a very small, submillimeter, region. Third, the spectra of the harmonics are expected to provide useful information on the dynamics of electron motion in CNs.

Consider an infinitely long single-shell CN oriented along the z axis and illuminated by an intense subpicosecond optical pulse with the carrier frequency ω_1. Let the pulse be incident normally to the CN's axis and polarized along this axis: $\mathbf{E}(x,t)=\mathbf{e}_z E_z(x,t)$. The CN geometry is conventionally classified by the integer-valued dual index (m,n) [2], which determines the direction of the plane graphite sheet when it rolls up into a cylinder. In a theoretical treatment we restrict ourselves to the zigzag CNs whose index is $(m,0)$ and whose radius is given by $R_{CN}=\sqrt{3}mb/2\pi$, where $b=1.42$ Å is the interatomic distance in a graphite sheet. A zigzag CN exhibits metallic properties when $m=3q$ with q as an integer. The analysis can easily be extended to armchair CNs, which are characterized by the index (m,m) and are metallic at any m. Assuming the high-order harmonic fields to be sufficiently weak, we neglect the role of high-order harmonics in the

electron dynamics. We also neglect the transverse current on the CN surface, considering the axial current to be predominant. In that case we can presume the propagation of high-order harmonics to be normal to the CN's axis, i.e., along the x axis. Then, neglecting the spatial dispersion in the charge carrier motion, we can describe this motion by the Boltzmann equation in the form as follows:

$$\frac{\partial f}{\partial t}-\frac{e}{c}\frac{\partial \mathbf{A}}{\partial t}\frac{\partial f}{\partial \mathbf{p}}=\nu[F(\mathbf{p})-f(\mathbf{p},t)], \tag{1}$$

with e as the electron charge and ν as the relaxation frequency. The initial condition is assumed to be $f(\mathbf{p},0)=F(\mathbf{p})$. A typical value of ν in CNs is $\nu\approx 10^{12}$ Hz [16]. The Fermi equilibrium distribution function $F(\mathbf{p})$ is given by $F(\mathbf{p})=\{1+\exp[\mathcal{E}(\mathbf{p})/k_BT]\}^{-1}$, where k_B is the Boltzmann constant, T is the temperature, and $\mathcal{E}(\mathbf{p})$ is the quantum-mechanical dispersion law for electrons in the CN. The vector-potential $\mathbf{A}$ is related to the electric field by the equation $\mathbf{E}=-(1/c)\partial\mathbf{A}/\partial t$. Further, we impose the restriction $\nu \ll \Delta\omega \ll \omega_1$ on the pulse bandwidth $\Delta\omega$. This allows us, on the one hand, to make use of the slowly varying envelope approximation and, particularly, the traveling-wave model for the driving field, $E_{z1}=E_1\cos(k_1x-\omega_1t)$. On the other hand, the above inequality leads to the approximate solution of Eq. (1), $f(\mathbf{p},t)\approx F(\mathbf{p}+e\mathbf{A}/c)$ [17]. In view of that, the current density in a single CN can be presented by

$$j_z=\frac{2e}{(2\pi\hbar)^2}\int\int_{1stBZ} v_z^{(e)}(\mathbf{p})F\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)d\mathbf{p}, \tag{2}$$

where $v_z^{(e)}(\mathbf{p})=\partial\mathcal{E}(\mathbf{p})/\partial p_z$ is the z component of the electron velocity. The abbreviation $1stBZ$ in Eq. (2) stands for the first Brillouin zone in the CN. A fundamental distinction of the CN from the plane monatomic graphite sheet is in the transverse quantization of the charge carrier motion [18]. Owing to this, the Brillouin zone of the graphite sheet, which is hexagonal, is transformed in CNs into a discrete population of straight lines inside the hexagon. In the tight-binding approximation, this results in the dispersion law of conduction electrons in zigzag CNs as follows [18]:

$$\mathcal{E}_s(\mathbf{p})=\pm\gamma_0\left[1+4\cos\left(\frac{3bp_z}{2\hbar}\right)\cos\left(\frac{\pi s}{m}\right)+4\cos^2\left(\frac{\pi s}{m}\right)\right]^{1/2} \quad (s=1,2,\ldots,m), \tag{3}$$

where γ_0 is the overlapping integral (for carbon $\gamma_0\approx 3$ eV), and the plus and minus correspond to conduction and valence bands, respectively.

Since the high-order harmonic intensity has been assumed to be small, we can identify the vector potential $\mathbf{A}$ in Eq. (2) with that of the driving field, $\mathbf{e}_zA_{z1}$. Then, expanding $\mathcal{E}_s(\mathbf{p})/\gamma_0$ and $F(\mathbf{p})$ in Eq. (2) into Fourier series with the Fourier coefficients $\mathcal{E}_{sq}$, F_{sq}, respectively, one can obtain the expression for the current as follows:

$$j_z=\tfrac{1}{2}j_0\sum_{s=1}^{m}\sum_{q=1}^{\infty} q\mathcal{E}_{sq}F_{sq}\sin\left(\frac{3be}{2\hbar c}A_{z1}q\right), \tag{4}$$

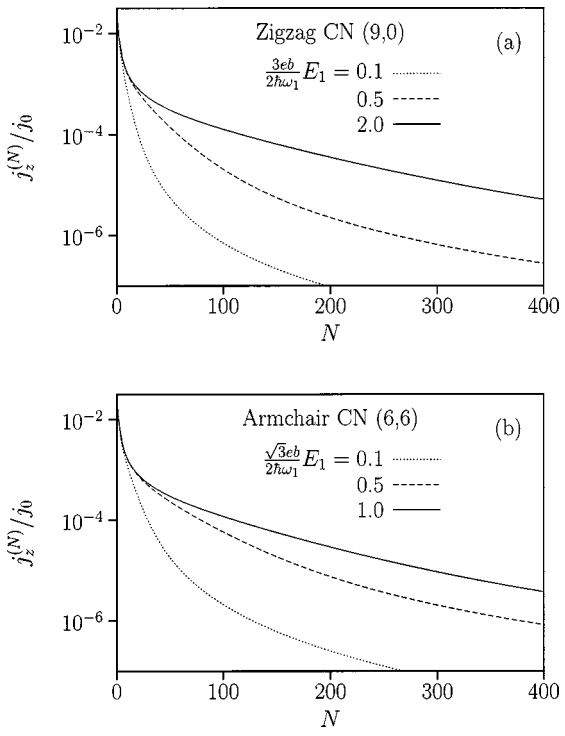

FIG. 1. High-order harmonic spectra of the nonlinear current induced in (a) metallic zigzag and (b) armchair CNs by different driving field strengths as indicated. The normalization is $j_0=5.2\times10^6$ A/m (a) and 4.6×10^6 A/m (b).

with $j_0=16e\gamma_0/\sqrt{3}\hbar mb$. Note that the Fourier coefficients are independent of the driving field, allowing us to separate the problem of their evaluation from the modeling of the current spectrum. In the traveling-wave model, $A_{z1}=(c/\omega_1)E_1\sin(k_1x-\omega_1t)$ and Eq. (4) results in

$$j_z=\sum_{M=0}^{\infty} j_z^{(2M+1)}\sin[(2M+1)(k_1x-\omega_1t)], \tag{5}$$

where

$$j_z^{(2M+1)}=j_0\sum_{s=1}^{m}\sum_{q=1}^{\infty} q\mathcal{E}_{sq}F_{sq}J_{2M+1}(\Lambda q), \tag{6}$$

$\Lambda=3beE_1/2\hbar\omega_1$, and $J_{2M+1}(\,)$ are the odd-order Bessel functions.

Equation (6) describes the HHG provided by the 2D-confined conduction electrons, which does not take into account intraband resonant transitions inherent in the CN lattice at optical frequencies. To estimate the limitation on the fundamental frequency imposed by the condition for resonant transitions to be negligible, a general approximate relation for the electron state density in a CN [19] can be applied that establishes the low-frequency edge of the optical transition band in metallic CNs: $\hbar\omega_1<3\gamma_0b/2R_{CN}$. This condition is decisive for the applicability of the developed theory of the HHG by 2D-confined conduction electrons in CNs. As the CN radius increases, the upper limit for the permissible fundamental frequency is shifted to the red. Thus, CNs with not too large radii are of the most interest. Computational results presented in Fig. 1 have been obtained for Ti:sapphire

laser emission as the driving field ($\lambda_1 = 0.8\ \mu$m) that satisfies this condition for chosen CNs. A second restriction is related to the strength of the driving field: the Stark frequency corresponding to this field must be smaller than the conduction zone bandwidth, $E_1 < \gamma_0/eb$ [17]. Otherwise, the bond of π electrons with the crystalline lattice breaks down, resulting in a strong Stark broadening and making the dispersion law (3) inapplicable. Note also that our theory ignores the role of σ electrons that come to play where the high-order harmonic frequencies $\omega_N = N\omega_1$ $(N = 2M+1)$ become comparable with the frequencies of corresponding transitions. Having resonant character, these transitions can disturb the high-order harmonic spectrum (5) in a restricted number of narrow bands.

Figure 1(a) demonstrates typical high-order harmonic spectra of the current in the single (9,0) zigzag CN calculated by Eq. (6) for different values of the parameter Λ. For $\lambda_1 = 0.8\ \mu$m, the magnitude $\Lambda = 1$ corresponds to the driving field strength $E_1 = 7.0 \times 10^9$ V/m or the field intensity $I = 1.3 \times 10^{13}$ W/cm^2. Our analysis has shown that the approximation that neglects the influence of the high-order harmonic fields on the electron motion is applicable at least for $\Lambda < 4\pi$. Figure 1(b) presents analogous results for the (6,6) armchair CN. A simple modification of the dispersion law [18] and the replacement $(\Lambda,\ j_0) \rightarrow (\Lambda/\sqrt{3},\ j_0/\sqrt{3})$ in Eq. (6) makes Eq. (5) applicable to this case. First, the pictures display a high efficiency of the HHG, allowing one to conclude that the metallic CNs are highly nonlinear systems in the IR and optical ranges. As the conduction electrons in metallic CNs offer a high density of states, the efficiency of high-order harmonic conversion falls off very slowly, extending with quite reasonable intensity to harmonic numbers as large as 400. Note also that for the given normalization coefficient the plots presented in the figure are weakly dependent on m and this dependence manifests itself only at high orders of harmonics. The following reasoning can explain this fact. The main contribution to the conductivity of metallic CNs at frequencies corresponding to low-order harmonics is provided by the Fermi electrons, the number of which is inversely proportional to m as long as the CN is metallic. Consequently, the ratio $j_z^{(N)}/j_0$ remains practically independent of m. From Eqs. (5) and (6), the equation of harmonic balance,

$$\sum_{M=0}^{\infty} (2M+1) j_z^{(2M+1)} = -\,\mathrm{Im}(\sigma_{zz}) E_1,$$

can readily be obtained, where σ_{zz} is the linear dynamical conductivity of the CN. In fact, the right-hand part of this equation is the linear current that would be induced by the given driving field in the linear structure with the conductivity σ_{zz}. For curves depicted in Fig. 1(a), the ratio $|j_z^{(1)}/\mathrm{Im}(\sigma_{zz}) E_1|$ ranges from 0.15 to 0.05. This shows the high efficiency of excitation of the current high harmonics by the driving field.

A significant peculiarity of the HHG in CNs is a smooth decrease of the conversion efficiency up to very high harmonic orders instead of a cutoff at a certain harmonic order. The cutoff effect is inherent in high-order harmonic spectra of an intense laser pulse interacting both with ionized gas [7–9] and solid targets [12–15]. Recent experiments with neon [9] localized the cutoff in the vicinity of the 49th harmonic, with a driving pulse intensity as large as 10^{14} W/cm^2. Our calculations show the extension of the HHG spectra in CNs far beyond this limit for a given driving intensity. Note also that the HHG in CNs produces only odd harmonics and turns out to be sensitive to the driving field polarization: only the field component parallel to the CN axis contributes to the process. This is because in CNs, different from the HHG provided by electrons oscillating across a sharp plasma-vacuum interface, the irradiation of high harmonics is produced by longitudinal oscillations of electrons.

The fact that the HHG spectra in metallic CNs do not exhibit the cutoff at a certain harmonic number can easily be understood by comparing with systems exhibiting the sinusoidal electron dispersion law that leads to $j_z^{(2M+1)} \sim J_{2M+1}(CE_1/\omega_1)$, with C as a constant. Such a dispersion law is characteristic of the BC_2N nanotube [4] as well as of lateral superlattices [20] comprising 2D arrays of quantum dots. The simplest two-level model of the intense pulse interaction with an ionized gas [21] also results in the above proportionality of the current harmonics. Mathematical properties of the Bessel functions explain a smooth plateau for low-order harmonics and a sharp cutoff at a certain number. The crucial distinction between the systems mentioned above and CNs arises from the specific electron dispersion law of the hexagonal crystalline structure. For the sinusoidal dispersion, only one spectral term contributes to the HHG, while dispersion law (3) produces an infinite number of spectral terms in Eq. (6) falling down slowly with q. As a result of their imposition, a sharp cutoff characteristic for everyone is blurred and transformed into a smooth decrease of the high-order harmonic conversion efficiency. It should be emphasized that the specific character of the electron dispersion in CNs is responsible for the unexpectedly strong nonlinearity made evident by our analysis. This feature drastically differentiates metallic CNs from bulk metals that exhibit a weak nonlinearity because of the parabolic dispersion law.

Thus, we have considered the process of HHG provided by nonlinear motion of 2D-confined electrons on the surface of metallic CNs and predict the strong nonlinearity of CNs and highly efficient HHG, which can be related to the dynamical localization of electrons in strong external fields. The high-order harmonic spectra predicted to be generated by CNs comprise the odd-order harmonics whose intensity smoothly falls off with harmonic number. In this paper we restricted ourselves to the HHG in a single metallic CN. A large number of CNs with a certain orientational statistics constitute a macroscopic sample, which can be highly anisotropic. For instance, a collection of aligned CNs can be treated as an uniaxial dielectric continuum, with its preferred axis parallel to the CN's axis [22]. Its pronounced anisotropy offers the possibility of meeting the phase-matching condition by varying the angle of incidence. The optimal angle depends on the harmonic order; e.g., there exists a mechanism to tune the radiation frequency to a desired value. Note that such a mechanism is not provided by other methods of HHG in both ionized gases and solid targets. Consideration

of this problem as well as the discussion of the HHG in semiconducting zigzag CNs will be given separately.

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