PHYSICAL REVIEW B VOLUME 50, NUMBER 5 1 AUGUST 1994-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Harmonic generation by a one-dimensional conductor: Exact results

Kirill A. Pronin* and André D. Bandrauk
Laboratoire de Chimie Théorique, Faculté des Sciences, Université de Sherbrooke, Quebec, Canada J1K 2R1

Alexander A. Ovchinnikov
Institute of Chemical Physics, Russian Academy of Sciences, Kosygin Street 4, 11977, Moscow, Russia

(Received 15 March 1994; revised manuscript received 18 May 1994)

The exact harmonic-generation (HG) spectrum is obtained analytically for a one-band one-dimensional conductor for both ac and ac + dc external fields. It is shown that even and odd harmonics can be created and controlled depending on the initial-state conditions and the field amplitudes E. The HG spectrum forms a single *plateau* with a cutoff defined by a maximum HG order N_m corresponding to the maximum energy acquired by the electron in the laser field. This maximum energy corresponds to single transfer between neighboring sites, i.e., $N_m = eEa/\hbar\omega$, where a is the lattice constant and ω the field frequency.

Quasi-one-dimensional (1D) systems such as conjugated polymers exhibit unusual anisotropic electric and optical properties due to a high degree of anisotropic electron delocalization along stacked molecular chains. Thus, high values of $\chi^{(3)}$, the third-order nonlinear optical (NLO) susceptibility, and ultrashort response times have been observed in various conjugated polymers.[1,2] Theoretical calculations of conductivity and NLO susceptibilities are usually of perturbative nature. Analytic or numerical results are rather few and are limited to one-electron approaches.[3-13] $\chi^{(3)}$ has been obtained previously analytically in the dc limit.[3,4] Field-theoretical models with a linearized electron spectrum have been also solved by the diagrammatic method to give general analytic expressions for $\chi^{(3)}$ for both degenerate and nondegenerate conjugated polymers,[5-9] $(AB)_x$ polymers,[9] and also for discrete Su-Schrieffer-Heeger models.[10,11] Extensions to higher-order susceptibilities have, to our knowledge, not been presented previously. On the other hand, current research in atomic and molecular physics deals with high-order harmonic generation (HG),[14-17] where theoretical and numerical nonpeturbative simulations have shown the existence of *plateaus* in HG spectra defined by sharp *cutoffs*, i.e., a maximum HG order followed by a sharp decrease in intensity. Such cutoffs are rationalized in terms of the maximum energy an electron can acquire in a laser field[14-17] in the presence of matter.

In this paper we calculate analytically and exactly the HG spectrum in ac and ac+dc fields for a one-band one-dimensional conductor. A well-defined plateau in the HG spectrum is also obtained, with a cutoff at the maximum HG order or photon number $N_m \approx eEa/\hbar\omega$, where E is the field amplitude, a the lattice spacing, and ω the photon frequency. *Even* and *odd* harmonic intensities are initial state dependent. These results are similar to previous two-state models[15] and HG in the H_2^+ molecule.[16,17] However, these results are totally unexpected as the systems are quite different.

We consider an infinite 1D chain in the tight-binding approximation with nearest-neighbor transfer integral V in a localized Wannier basis set $|n\rangle$ under the influence of an arbitrary time-dependent electric field $E(t)$:

$$H(t) = -V\sum_n (|n\rangle\langle n+1| + |n+1\rangle\langle n|) + eE(t)\sum_n n|n\rangle\langle n|. \tag{1}$$

The intersite distance a is the unit of length and the electron charge is $-e$. The substitution

$$c_n(t) = \tilde{c}_n(t)\exp[-in\eta(t)], \qquad \eta(t) = e\hbar^{-1}\int_0^t dt' E(t'), \tag{2}$$

in the time-dependent Schrödinger equation for $|\varphi(t)\rangle = \Sigma c_n(t)|n\rangle$, where $\eta(t)$ is the exact field area,[16] eliminates in the Hamiltonian (1) the radiative interaction giving the resulting Schrödinger equation for the new coefficients $\tilde{c}_n(t)$,

$$i\hbar\frac{\partial}{\partial t}\tilde{c}_n(t) = -V[e^{i\eta(t)}\tilde{c}_{n-1}(t) + e^{-i\eta(t)}\tilde{c}_{n+1}(t)]. \tag{3}$$

Equation (3) can be readily solved with the help of Fourier transforms, generating functions for Bessel functions J_n, and Graf's addition theorem,[19] to give finally,[20]

$$c_n(t)=e^{-in\eta(t)}\sum_r c_r(0)J_{n-r}(2|s|)\left[i\frac{s}{|s|}\right]^{n-r},$$
$$s=\frac{V}{\hbar}\int_0^t dt' e^{i\eta(t')}. \tag{4}$$

s is a new variable involving exponentiation of the field area $\eta(t)$. A similar expression had been obtained earlier in studies of dynamic localization.[21] One can now define the average dipole moment per unit volume as in Ref. 18 or polarizability p,

$$d(t)=-e\sum n\rho_{n,n}(t),\quad p(t)=N^{-1}d(t),\quad N\to\infty, \tag{5}$$

where $\rho_{n,n}(t)$ is the density matrix. Then with the help of Eq. (4) and after lengthy calculation,[20] we find the following expressions for the average induced dipole moment $\Delta d(t)$ and the second time derivative $\ddot{d}(t)$ (i.e., the electron acceleration),

$$\Delta d(t)=d(t)-d(t=0)=2e\rho\frac{V}{\hbar}\int_0^t dt'\sin[\eta(t')-\kappa], \tag{6}$$

$$\ddot{d}(t)=2e\rho\frac{VeE(t)}{\hbar^2}\cos[\eta(t)-\kappa]. \tag{7}$$

The parameters ρ and κ are determined by the elements of the initial density matrix $\rho_{n,n}(t)$ thus defining the initial-state conditions,

$$d(0)=-e\sum_n n\rho_{n,n}(0),\quad \rho e^{i\kappa}=\sum_n \rho_{n,n+1}(0). \tag{8}$$

Equations (6)–(8) provide *exact* and most general solutions for the electron response to any arbitrary external perturbation $E(t)$.[20]

We now consider the specific case of response to a harmonic ac field,

$$E(t)=E\cos(\omega t),\quad \varepsilon=eE/\hbar\omega,\quad \eta(t)=\varepsilon\sin(\omega t). \tag{9}$$

The resulting induced dipole moment (6) becomes

$$\Delta d(t)=-2e\rho\frac{V}{\hbar}t\sin(\kappa)J_0(\varepsilon)+2e\rho\frac{V}{\hbar\omega}\varepsilon\cos(\kappa)\,{}_1F_2\left(1;\frac{3}{3},\frac{3}{2};-\frac{\varepsilon^2}{4}\right)-4e\rho\frac{V}{\hbar\omega}\left[\cos(\kappa)\sum_0^\infty J_{2\nu+1}(\varepsilon)\frac{\cos[(2\nu+1)\omega t]}{2\nu+1}\right.$$
$$\left.+\sin(\kappa)\sum_1^\infty J_{2\nu}(\varepsilon)\frac{\sin[2\nu\omega t]}{2\nu}\right]. \tag{10}$$

where ${}_1F_2$ is a hypergeometric function. The corresponding expansion of the acceleration form of the polarization (7) reads

$$\ddot{d}(t)=4e\rho\frac{V}{\hbar}\omega\left[\cos(\kappa)\sum_0^\infty J_{2\nu+1}(\varepsilon)(2\nu+1)\cos[(2\nu+1)\omega t]+\sin(\kappa)\sum_1^\infty J_{2\nu}(\varepsilon)2\nu\sin[2\nu\omega t]\right]. \tag{11}$$

The electron acceleration form (11) enters as a source term in Maxwell's equations.[18] We note that the acceleration (11) is devoid of any constant, i.e., time-independent component, contrary to the dipole expression (10). Such constant dipole moment creates large background HG contributions in numerical computations.[16,22] In Fig. 1 we present a numerical example of Eq. (11) for the power spectrum $P(\omega)=|\int_0^T\ddot{d}(t)e^{i\omega t}d\omega/T|^2$. Both even and odd harmonics appear with a sharp cutoff at around $N_m=15$, i.e., the highest harmonic order.

We now exhibit the initial-state dependence of the HG spectrum. Thus for an initial one-electron eigenstate, i.e., a Bloch wave, then from Eqs. (8) we have the simple result $\rho=1$, $\kappa=k$, where k is the initial wave vector. The first term in the dipole (10) represents the linear growth of the dipole moment due to the propagation of the Bloch wave with an average velocity $v=(2V/\hbar)J_0(\varepsilon)\sin k$, where $J_0(\varepsilon)$ is a zero-order Bessel function with argument $\varepsilon=eE/\hbar\omega$, representing the average effect of the harmonic field on the electron velocity during one period. This same Bessel function defines the field-induced Floquet energy separation for two-level models.[15] The second term in (10) compensates for the nonzero component of the first odd Fourier sum at $t=0$. clearly even and odd harmonics are of comparable magnitude if the electron in the band occupies initially Bloch states with $k=\pm\pi/4$, $\pm3\pi/4$. Only *even* harmonics appear for $k=\pm\pi/2$ and there are only *odd* harmonics for $k=0,\pm\pi$. In the latter case the linearly growing dipole term in (11) also vanishes.

We next consider a partially filled band, i.e., a *metal*, with $\nu=2k_f/\pi$ electrons per atom where k_f is the Fermi wave vector. From (8) we have the succinct results,

$$N_e=\sum_n \rho_{nn}(0)=2N\pi^{-1}k_F,\quad \rho\sin\kappa=0,$$
$$\rho\cos\kappa=2N\pi^{-1}\sin k_F, \tag{12}$$

where N_e is the total number of electrons for N sites. For this

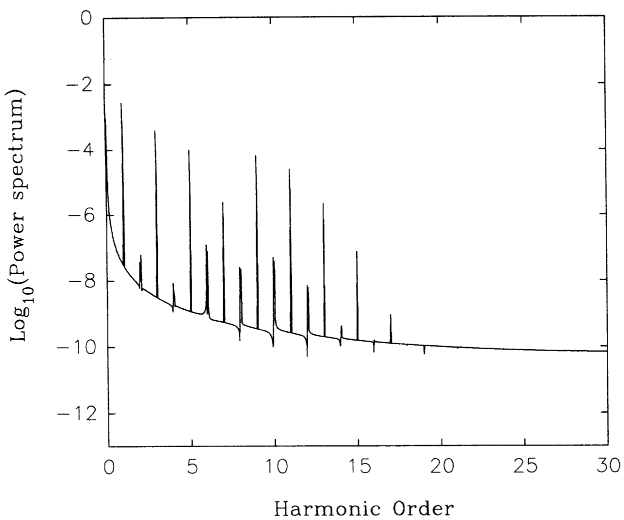

FIG. 1. Power spectrum $P(\omega)=|\omega^2 d(\omega)|^2$ from Eq. (11) for $eEa/\hbar\omega=15$ and $\kappa=\pi/10$. Sharp cutoff at $N_m=15$ corresponds to maximum harmonic generation order.

case, the linear dipole term in (10) and the amplitudes of *even* harmonics all vanish. For large field amplitudes (intensities) and (or) low fundamental frequencies ω such that $\varepsilon \gg 1$, the HG amplitudes A_ν of order ν decrease slowly as ν^{-1}, forming a *plateau* in the spectrum. This can be readily ascertained from the Bessel function asymptotics[19] for $\varepsilon \gg \nu > 0$:

$$A_{2\nu}=-4e\frac{\rho V}{\hbar\omega}\left(\frac{2}{\pi\varepsilon}\right)^{1/2}\sin(\kappa)\cos(\varepsilon-\pi/4)\frac{(-1)^\nu}{2\nu}, \tag{13}$$

$$A_{2\nu-1}=-4e\frac{\rho V}{\hbar\omega}\left(\frac{2}{\pi\varepsilon}\right)^{1/2}\cos(\kappa)\cos(\varepsilon+\pi/4)\frac{(-1)^{\nu-1}}{(2\nu-1)}. \tag{14}$$

We note that for $\varepsilon=\pi/4+m\pi$ ($m=$integer), low-order *odd* harmonics can be made to vanish, whereas *even* harmonics will be suppressed at $\varepsilon=3\pi/4+m\pi$. The boundary or *cutoff* of the HG plateau predicted by (14) and (15) is characterized by the parameter $N_m \approx \varepsilon e/2$ ($\ln e=1$). For harmonic orders ν greater than N_m, the HG amplitudes decrease extremely rapidly in the limit $\nu \gg \varepsilon > 0$,

$$A_{2\nu}=-\frac{8e\rho V}{\pi^{1/2}\hbar\omega}\left[\frac{2}{e\varepsilon}\right]^{3/2}\left[\frac{e\varepsilon}{4\nu}\right]^{2\nu+3/2}\sin\kappa, \tag{15}$$

$$A_{2\nu-1}=-\frac{8e\rho V}{\pi^{1/2}\hbar\omega}\left[\frac{2}{e\varepsilon}\right]^{3/2}\left[\frac{e\varepsilon}{2(2\nu-1)}\right]^{2\nu+3/2}\cos\kappa, \tag{16}$$

For low-intensity or high-frequency fields such that $eE/\hbar\omega < 1$, the plateaus (13) and (14) and cutoffs (15) and (16) decrease rapidly as a function of the order ν. Thus favorable conditions for the observation of the HG plateaus correspond to large fields E and (or) low frequencies ω. As an example, Fig. 1 shows a cutoff at $N_m=15$ such that $N_m\hbar\omega=eEa$.

We finally consider the response of the 1D band conductor to a sum of constant and harmonic (dc+ac) electric fields,

$$E(t)=E_0+E\cos\omega t, \qquad \eta(t)=\omega_0 t+\varepsilon\sin\omega t, \tag{17}$$

where $\omega_0=eE_0/\hbar$ is the Bloch frequency for the dc field giving rise to the well-known Bloch oscillations.[23] Introducing the notation $\mu=\omega_0/\omega$, the ratio of the Bloch and harmonic frequencies, and defining the Anger function

$$J_\mu(\varepsilon)=\frac{1}{\pi}\int_0^\pi dt\cos(\mu t-\varepsilon\sin t), \tag{18}$$

then for *commensurate* values of ω_0 and ω so that $m\mu$ $=$integers, the field-induced dipole (6) can be expressed in terms of the Anger functions [for irrational values of $m\mu$, analytic expressions for $\Delta d(t)$ can be obtained only for particular periods of the field[20]],

$$\Delta d(t)=-2e\rho\frac{V}{\hbar}\left\{\Delta(\mu)\sin(\kappa)(-1)^\mu J_\mu(\varepsilon)t+\omega_0^{-1}J_0(\varepsilon)[\cos(\omega_0 t-\kappa)-\cos(\kappa)]\right.$$
$$\left.+\sum_{\nu=1}^{\infty}{}' J_\nu(\varepsilon)\left[\frac{\cos[(\nu\omega+\omega_0)t-\kappa]-\cos(\kappa)}{\nu\omega+\omega_0}-(-1)^\nu\frac{\cos[(\nu\omega-\omega_0)t+\kappa]-\cos(\kappa)}{\nu\omega-\omega_0}\right]\right\}. \tag{19}$$

[$\Delta(\mu)=1$ for μ-integer, $\Delta(\mu)=0$ otherwise.] The prime in the sum implies the omittance of terms with $\nu\pm\mu$ in the denominators of (19) if μ is integer thus eliminating divergences.

We note from (19) that the dc electric field provides a tool to *control* the HG spectrum. Thus the constant field splits each harmonic induced by the ac field into two peaks shifted by the Bloch frequency ω_0. Changing the dc field magnitude one changes the splitting uniformly for all harmonics. As in the ac case, Eqs. (13)–(16), the HG spectrum in the ac+dc case also reveals plateaus. For $\varepsilon \gg \nu > 0$, the HG amplitudes decrease as ν^{-1},

$$A_{\pm,\nu}=-2e\frac{\rho V}{\hbar\omega}\left(\frac{2}{\pi\varepsilon}\right)^{1/2}\frac{\cos(\varepsilon-\pi\nu/2-\pi/4)}{\nu\pm\mu}\left\{\begin{matrix}1\\(-1)^{\nu+1}\end{matrix}\right\}, \tag{20}$$

where $A_{\pm,\nu}$ is the amplitude of the νth harmonic in (19) with the upper (lower) sign corresponding to the sum (difference) of frequencies $\nu\omega$ and ω_0. As in (13) and (14) one can again control even and odd harmonics by choosing an appropriate ε. The position of the cutoff is characterized by the same parameter $N_m \approx \varepsilon$ as in the pure ac case [Eqs. (15) and (16)]. The HG amplitudes now decrease very rapidly for $\nu \gg \varepsilon > 0$ as

$$A_{\pm,\nu} \approx -2e\frac{\rho V}{\hbar\omega}\left(\frac{1}{2\pi\nu}\right)^{1/2}\frac{1}{(\nu\pm\mu)}\left[\frac{e\varepsilon}{2\nu}\right]^{\nu}\begin{Bmatrix}1\\(-1)^{\nu+1}\end{Bmatrix}. \tag{21}$$

Both examples of HG, i.e., ac and ac+dc fields, for a one-dimensional conductor exhibit plateaus which are ended at high order ν by a cutoff defined by the maximum order or photon number: $N_m = eEa/\hbar\omega$ ($a=1$ in our model) (see also Fig. 1). Such a cutoff occurs as well in two-level models[15] and in rigorous calculations of HG by the diatomic molecule H_2^+.[16,17] $eEa/\hbar\omega$ is the ratio of the energy gain of an electron transfer between neighboring sites to the photon energy. This turns out to be the maximum energy gain also for an electron in a 1D conductor subjected to a time-dependent electric field of amplitude E and frequency ω. Experimental verification of such cutoffs in the HG spectra of quasi-1D conductors would allow one to conclude whether electrons are restricted to single bands in the presence of laser fields.

We thank the Natural Sciences and Engineering Research Council of Canada for financing this research and Dr. T. Zuo for valuable advice and assistance.

*Permanent address: Institute of Chemical Physics, Russian Academy of Sciences.

[1] R. A. Hann and D. Bloor, *Organic Materials for Nonlinear Optics* (Royal Chem. Soc., London, 1989).
[2] D. Baeriswyl, D. K. Campbell, and S. Mazumdar, in *The Physics of Conducting Polymers*, edited by H. Kriess (Springer-Verlag, Berlin, 1991).
[3] H. F. Hameka, J. Chem. Phys. **67**, 2935 (1977).
[4] C. Cojan, G. P. Agrawal, and C. Flytzannis, Phys. Rev. B **15**, 909 (1977); **17**, 776 (1978).
[5] K. Fesser, A. R. Bishop, and D. K. Campbell, Phys. Rev. B **27**, 4804 (1983).
[6] T. Martin and D. K. Campbell, Phys. Rev. B **35**, 7732 (1987).
[7] W. Wu, Phys. Rev. Lett. **61**, 1119 (1977).
[8] K. A. Pronin and Y. I. Dakhnovskii, Synth. Met. **41-43**, 3759 (1991).
[9] Y. I. Dakhnovskii and A. D. Bandrauk, Synth. Met. **41-43**, 3747 (1991).
[10] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **32**, 2099 (1980).
[11] K. A. Pronin, Y. I. Dakhnovskii, and A. D. Bandrauk, Synth. Met. **55-57**, 3907 (1993).
[12] J. Yu, B. Friedman, P. R. Baldwin, and W. P. Su, Phys. Rev. B **39**, 12 814 (1989).
[13] J. E. Sipe and E. Ghahramani, Phys. Rev. B **48**, 11 705 (1993).
[14] J. L. Krause, K . J. Schafer, and K. C. Kulander, Phys. Rev. A **45**, 4998 (1992).
[15] Y. Ivanov and P. B. Corkum, Phys. Rev. A **48**, 580 (1993).
[16] T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A **48**, 3837 (1993).
[17] T. Zuo, S. Chelkowski, and A. D. Bandrauk, Phys. Rev. A **49**, 3943 (1994).
[18] Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1984).
[19] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
[20] K. A. Pronin, A. D. Bandrauk, and A. A. Ovchinnikov (unpublished).
[21] D. H. Dunlap and V. M. Kenkre, Phys. Rev. B **34**, 3625 (1986).
[22] K. Burnett, C. V. Reed, J. Cooper, and P. L. Knight, Phys. Rev. A **45**, 3347 (1992).
[23] G. Nenciu, Rev. Mod. Phys. **63**, 91 (1991).