Nonlinear Optical Susceptibilities of a One-Dimensional Semiconductor

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By use of the Keldysh nonequilibrium Green's-function methods, analytic expressions are computed for the nonlinear optical susceptibilities for the one-dimensional semiconductor model of a conducting polymer. The model has no adjustable parameter. The results for third-harmonic generation are in excellent agreement with experiments on polyacetylene. Further nonlinear optical effects, which should be experimentally observable, are predicted. The physical significance of these results is discussed.

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Recently, considerable experimental attention has been focused on the nonlinear optical properties of conducting polymers. Conducting polymers exhibit novel nonlinear optical properties. In particular, there are major shifts in oscillator strength within picoseconds after absorption of photons.[1] Also, a large third-order optical susceptibility, $\chi^{(3)}$, has been observed in polyacetylene.[2,3] These observations indicate that conducting polymers might have applications as fast nonlinear optical materials.

On the theoretical side, there is persistent debate about the strength of the electron-electron interactions in conducting polymers. In Ref. 4, it was shown that a picture of weakly interacting quasiparticles provides a consistent theory of conducting polymers. The predictions of the theory are in fairly good agreement with all previous experimental observations. Since the strongly and weakly correlated systems behave very differently in many ways, particularly in their responses to an external optical field, it is natural to ask whether or not the same theory can predict the spectrum of the nonlinear optical susceptibility measured in polyacetylene.[2]

There are two types of elementary excitations which are related to the optical responses of the system: (i) charge excitations which occur in one-photon processes and (ii) neutral excitations which involve two-photon processes. Thus, the two-photon processes involved in the nonlinear responses will enable one to access the neutral excitations which are not accessible (because of a selection rule) to one-photon processes. The relative position of the gap to charge excitations (Δ_c) and the gap to neutral excitations (Δ_n) depends upon the strength of the electron-electron interactions in the system.[5-8] For the strongly correlated system $\Delta_c \gg \Delta_n$, while for the weakly correlated system $\Delta_c \approx \Delta_n$. Thus, the strongly and weakly correlated systems have distinct qualitative signatures in their nonlinear optical responses. For the strongly correlated system, we expect that the one-photon resonance occurs at much higher energy than the two-photon resonance. In contrast, for the weakly correlated system, the one-photon resonance energy should be close to n times the n-photon resonance energy. Therefore, a detailed study of the nonlinear optical responses of conducting polymers will provide another stringent test of the role of electron-electron correlation effects. In this Letter, I investigate the nonlinear response of conducting polymers in the framework of a independent quasiparticle model as a first step towards understanding the large nonlinear optical susceptibility of this class of quasi-one-dimensional systems.

Because of the great complexity of the calculations, few explicit calculations of the nonlinear optical susceptibilities have been performed.[9] I am not aware of any analytic calculations over the full frequency range which have been carried out for realistic models based on a systematic analysis of the appropriate response theory. Here I derive the general formalism of nonlinear optical susceptibilities from the Keldysh nonequilibrium Green's-function method.[10]

The nth-order nonlinear optical susceptibility, $\chi^{(n)}(\Omega;\omega_1,\ldots,\omega_n)$, is related to nth-order current-current correlation function, $\chi_{jj}^{(n)}(\Omega;\omega_1,\ldots,\omega_n)$, according to

$$\chi^{(n)}(\Omega;\omega_1,\ldots,\omega_n)=\frac{\chi_{jj}^{(n)}(\Omega;\omega_1,\ldots,\omega_n)}{\Omega\omega_1\cdots\omega_n}, \tag{1}$$

where $\Omega \equiv -\sum_{i=1}^{n}\omega_i$, and

$$\chi_{jj}^{(n)}(\Omega;\omega_1,\ldots,\omega_n)\equiv\left[\frac{-i}{\hbar}\right]^n\frac{1}{n!}\int d^3x_1\cdots d^3x_n\int dt_1\cdots dt_n\int d^3x\,dt\,e^{-i\mathbf{k}\cdot\mathbf{x}+i\Omega t}\langle T_c j(x,t)j(x_1,t_1)\cdots j(x_n,t_n)\rangle, \tag{2}$$

with T_c the time-ordering operator along the Keldysh contour[10] and $j(x,t)$ the current operator.

Expressing the nonlinear susceptibilities in terms of Keldysh time-ordered current-current correlation functions has great advantage over the conventional formalism. The current-current correlation functions in Eq. (2) can be calculated with Keldysh Green's functions and Feynman diagrams similar to those in equilibrium many-body problems. This simplifies the calculations to a great extent.

Since we have previously argued that most conducting polymers are weakly correlated systems,[1,4] I take the noninteracting one-dimension model[11] as the unperturbed Hamiltonian H_0, and couple it to a time-dependent external electromagnetic field. The resulting Lagrangian density is

$$L=\psi^\dagger(x)\{i\hbar\,\partial_t-e\phi-\sigma_3 v_F[-i\partial_x-eA(x)/c]\}\psi(x)+\Delta\psi^\dagger(x)\sigma_1\psi(x). \tag{3}$$

The charge and current densities are given by

$$\rho(x)=\psi^\dagger(x)\psi(x), \tag{4}$$

$$j(x)=v_F\psi^\dagger(x)\sigma_3\psi(x), \tag{5}$$

where $\psi^\dagger(x)=(\psi_1^\dagger(x),\psi_2^\dagger(x))$ is the two-component spinor describing the left-going and right-going electrons, v_F is the Fermi velocity, and Δ is the energy gap between the valence and conducting bands. $\phi(x)$ and $A(x)$ are the scalar and vector potentials characterizing the external electromagnetic field; the σ's are the Pauli matrices. The model described by Eq. (3) is the simplest model of a one-dimensional semiconductor, and neglects dynamic electron-phonon and electron-electron interactions. The effects of these interactions are the subjects of ongoing investigations. I emphasize that the only parameter in the model is the gap, Δ, which can be determined independently from the linear optical response measurement. Therefore, there is no adjustable parameter in the model.

The third-order optical susceptibility, $\chi^{(3)}(\Omega;\omega_1,\omega_2,\omega_3)$, is proportional to the four-current correlation function $\chi_{jj}^{(3)}(\Omega;\omega_1,\omega_2,\omega_3)$ as in Eq. (1). Following the Feynman rules,[10,12] we have

$$\chi_{jj}^{(3)}(\Omega;\omega_1,\omega_2,\omega_3)=(-2)\left(\frac{-i}{\hbar}\right)^3 e^4 v_F^4\sum_{l,m,n=1}^{2}\int \mathrm{Tr}[\sigma_3 G_{1l}(k,\omega)\sigma_3 G_{lm}(k,\omega-\omega_1)$$
$$\times\sigma_3 G_{mn}(k,\omega-\omega_1-\omega_2)\sigma_3 G_{n1}(k,\omega-\omega_1-\omega_2-\omega_3)]\frac{dk\,d\omega}{(2\pi)^2}, \tag{6}$$

where $G_{ij}(k,\omega)$ are components of the Keldysh Green's functions.[6]

From the Lagrangian (3) and the definitions of the Keldysh Green's functions, one can readily calculate these Green's functions:

$$G_{11}(k,\omega)=\frac{\omega+v_F k\sigma_3+\Delta\sigma_1/\hbar}{\omega^2-\omega_k^2+i\eta}, \tag{7}$$

$$G_{22}(k,\omega)=-\frac{\omega+v_F k\sigma_3+\Delta\sigma_1/\hbar}{\omega^2-\omega_k^2-i\eta}, \tag{8}$$

$$G_{12}(k,\omega)=\frac{i\pi}{\omega_k}\left(\omega_k-v_F k\sigma_3-\frac{\Delta\sigma_1}{\hbar}\right)\delta(\omega+\omega_k), \tag{9}$$

$$G_{21}(k,\omega)=-\frac{i\pi}{\omega_k}\left(\omega_k+v_F k\sigma_3+\frac{\Delta\sigma_1}{\hbar}\right)\delta(\omega-\omega_k), \tag{10}$$

where $\omega_k\equiv[(v_F k)^2+(\Delta/\hbar)^2]^{1/2}$ and $\eta\equiv 0^+$.

First let us calculate the third-harmonic generation (THG); i.e., we take $\omega_1=\omega_2=\omega_3=\omega$ in Eq. (6). The calculations are very tedious. Fortunately, they can be done exactly. For a system which consists of chains in a parallel array, the THG is

$$\chi_{\mathrm{THG}}^{(3)}(\omega)\equiv\chi^{(3)}(-3\omega;\omega,\omega,\omega)=\frac{B_1}{z^8\epsilon_0^3}\{3(1-8z^2)f(3z)-8(1-4z^2)f(2z)+(5-8z^2)f(z)\}, \tag{11}$$

with $B_1\equiv e^4(\hbar v_F)^3 a/1152\pi\Delta^6 v$, where

$$f(z)\equiv\begin{cases}\dfrac{\arcsin(z)}{z(1-z^2)^{1/2}} & z^2<1,\\[2ex] \dfrac{1}{(z^2-1)^{1/2}}\left(-\dfrac{i\pi}{2z}-\dfrac{\cosh^{-1}z}{|z|}\right) & z^2>1,\end{cases} \tag{12}$$

and $z\equiv\hbar\omega/2\Delta$. a is the lattice constant and v is volume of the unit cell; $\hbar v_F=Wa$, and W is the bandwidth. For polyacetylene, $B_1\sim 1\times 10^{-12}$ esu.

The calculated $\chi_{\mathrm{THG}}^{(3)}(\omega)$ is plotted in Fig. 1. It exhibits a divergence at $3\hbar\omega=2\Delta$ which comes from the three-photon resonance enhancement. In order to com-

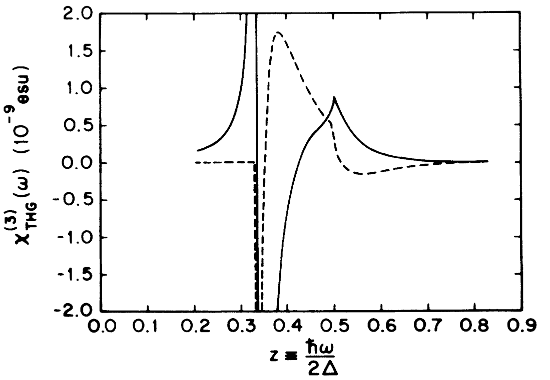

FIG. 1. The real (sold line) and imaginary (dashed line) parts of $\chi^{(3)}_{THG}(\omega)$.

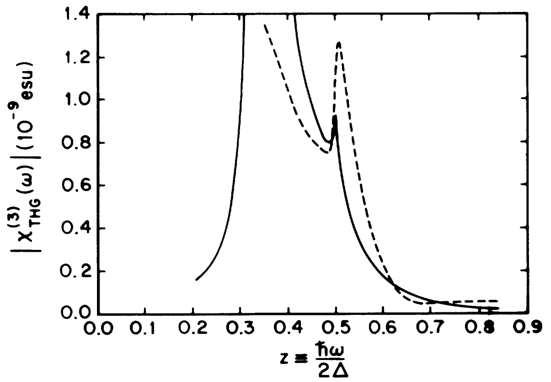

FIG. 2. The theoretical (solid line) and experimental (dashed line) $|\chi^{(3)}_{THG}(\omega)|$.

pare with experiment, I plot the calculated $|\chi^{(3)}_{THG}(\omega)|$ together with the experimentally measured one (Ref. 2) in Fig. 2. The calculated spectral features are in excellent agreement with experiment. A very surprising feature is the existence of a peak starting at $\hbar\omega = \Delta$. This peak has been observed[2] experimentally. It cannot be a two-photon resonance enhancement because in the rigid-band semiconductor model which I have adopted, two-photon absorption is forbidden by momentum conservation. This can be seen explicitly in Eq. (11). The coefficient of $f(2z)$ is proportional to $1-4z^2$ which vanishes for $z=\frac{1}{2}$, i.e., $\hbar\omega = \Delta$. Though the transition matrix element vanishes exactly at $\hbar\omega = \Delta$, it is finite away from that particular energy. In the neighborhood of $\hbar\omega = \Delta$, the smallness of the energy difference in the denominator contributes to the observed peak. Therefore, this peak is due to a large polarizability at that energy. As we can see from Fig. 1, this peak comes mainly from the real part of $\chi^{(3)}_{THG}(\omega)$ instead of the imaginary part.

The intensity-dependent index of refraction (IDIR), $\chi^{(3)}_{IDIR}(\omega)$, has also been computed. I get

$$\chi^{(3)}_{IDIR}(\omega) \equiv \tfrac{1}{3}[\chi^{(3)}(-\omega;-\omega,\omega,\omega)+\chi^{(3)}(-\omega;\omega,-\omega,\omega)+\chi^{(3)}(-\omega;\omega,\omega,-\omega)]$$
$$= \frac{B_2}{z^8}\left\{(1-4z^2)f(2z) - \frac{(1-4z^2)}{2(1-z^2)^2}z^2 + \frac{8z^6-12z^4+9z^2-2}{2(1-z^2)^2}f(z)\right\}, \qquad (13)$$

where $f(z)$ and z are defined as before, and $B_2 \equiv e^4(\hbar v_F)^3 a/48\pi\Delta^6 v$. For polyacetylene, $B_2 \sim 2\times 10^{-11}$ esu.

Again, momentum conservation implies that there is no absorption at the two-photon threshold and hence is responsible for the factor $1-4z^2$ which multiplies $f(2z)$; i.e., the two-photon resonance is suppressed.

The intensity-dependent index of refraction, $\chi^{(3)}_{IDIR}(\omega)$, is plotted in Fig. 3. $\chi^{(3)}_{IDIR}(\omega)$ is roughly the same order of magnitude as $\chi^{(3)}_{THG}(\omega)$. From Fig. 3, we see that $\mathrm{Im}\chi^{(3)}_{IDIR}(\omega)$ has a finite peak near $z=\frac{1}{2}$. I predict that a two-photon absorption experiment should be able to observe this peak. Another important feature of $\chi^{(3)}_{IDIR}(\omega)$ is the large $\mathrm{Re}\chi^{(3)}_{IDIR}(\omega)$ over a wide frequency range. Particularly, it is large when $\mathrm{Im}\chi^{(3)}_{IDIR}(\omega)$ is small. This means that these conducting polymers will display large changes in their index of refraction under intense laser illumination.

The result on $\mathrm{Im}\chi^{(3)}_{IDIR}(\omega)$ agrees with the numerical result on a discrete model obtained by Agrawal, Cojan, and Flytzanis.[9] Therefore, both continuum and discrete models produce the same spectral features as expected.

In this Letter I have shown that the Keldysh nonequilibrium Green's-function method provides the most practically useful scheme to calculate the nonlinear susceptibilities. The significance of the results in the field of conducting polymers can be summarized as follows: (1) I have identified the qualitative differences in optical responses for strongly and weakly correlated systems.

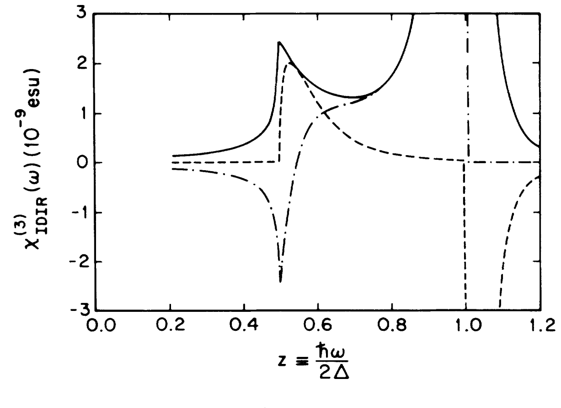

FIG. 3. The computed $\chi^{(3)}_{IDIR}(\omega)$. The dot-dashed line is the real part; the dashed line is the imaginary part; and the solid line is the magnitude.

The third-order optical susceptibilities of the noninteracting model clearly show resonance features at photon energies near $\frac{1}{3}\Delta_c$, $\frac{1}{2}\Delta_c$, and Δ_c. The excellent agreement between experiment and theory is a strong evidence that polyacetylene is well described in terms of weakly interacting quasiparticles.[13] (2) The large nonlinear optical susceptibilities in conducting polymers make these materials very promising candidates for fast nonlinear optical materials. In particular, the calculated intensity-dependent index of refraction $\chi^{(3)}_{\mathrm{IDIR}}(\omega)$ has a large real part over a wide range of frequencies. Most importantly, it is very large even where there is little absorption. This feature indicates that these materials may be high-quality nonlinear optical materials. Experimental verification of these features would certainly be very exciting. Further effects, such as perturbative effects of the dynamic electron-phonon interaction, can also be explored within the Keldysh formalism. Since the two-photon resonance is suppressed in the noninteracting limit as a result of momentum conservation, I expect that the major effect of electron-phonon coupling will be to act as a momentum sink, and hence enhance the two-photon peak. I am currently studying this problem.

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[13] Of course, one cannot completely rule out the possibility that the resonances reflect different excitations and the 2:3 ratio is fortuitous. However, since the model does not have any adjustable parameters, the chance of magical coincidence is quite low.