Resonant ultrafast nonlinear optics of bulk semiconductors under electric-field modulation

Chih-Ming Lai

Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan

Hsin-Fei Meng*

Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan

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In bulk direct-band-gap semiconductors the ground state of a (photoexcited) electron-hole system is normally an exciton gas, instead of an electron-hole plasma, as long as the carrier density is not too large. We demonstrate theoretically that, in the presence of an electric-field modulation, the energy of the plasma is decreased due to the induced charge-density fluctuation. As a results, the plasma becomes the ground state at much lower carrier densities, implying that the critical carrier density for the transition between these two states can be reduced. This transition provides a mechanism of nonlinear optics for bulk direct-band-gap semiconductors with picosecond relaxation time, large nonlinearity, and low pump intensity.
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I. INTRODUCTION

The mechanisms for the intensity-dependent refractive index, i.e., the optical Kerr effect, have been an important subject for research in nonlinear optics. The application of the Kerr effect on, among other things, all-optical switching has been one of the principle motivations. Therefore, not only the nonlinearity, but also the relaxation time, is a factor of primary importance. For resonant nonlinearities, whose Kerr effect is usually due to the absorption changes induced by the photoexcited quasiparticles, one faces a trade-off between these two factors. The relaxation is limited by the lifetime of the excited quasiparticles. However, any mechanism that reduces the quasiparticle lifetime frequently lowers the concentration of the quasiparticles for a given excitation intensity and consequently diminishes the nonlinearity. On the other hand, enhancing the nonlinearity by increasing the lifetime will reduce the switching speed. In practice, the radiative lifetime of the quasiparticles usually sets the ultimate limit for the switching time. For example, GaAs multiple quantum wells (MQW's) exhibit a large Kerr effect because the exciton absorption peak is bleached by the presence of other excitons already excited, due to phase-space filling (PSF) effect.[1] The switching time of high-quality MQW's is the lifetime of the excitons, which is typically a few nanoseconds.[2] In this paper we present a mechanism for resonant nonlinearity in bulk direct band-gap semiconductors under external electric-field modulation, which does not suffer from the nonlinearity-relaxation trade-off. This is possible because the relaxation time of this mechanism is not limited by the quasiparticle lifetime. Instead, it is only limited by the transition time between two different collective states of the quasiparticles: the electron-hole (*e-h*) plasma (EHP) and the exciton molecular gas (EMG). Large nonlinearity results from the distinct optical properties of the two states.

Take GaAs as an example first. The nonlinear effect of bulk GaAs is appreciable only at very high excitation powers.[3] For bulk GaAs, the principle mechanism for the exciton peak bleaching is the plasma screening of the Coulomb attraction between the electrons and holes. However, under resonant excitations and at low temperatures, the EHP is formed only when the carrier density is as high as 10^{17} cm^{-3},[4,5] while the relaxation is still limited by the nanosecond exciton lifetime. For indirect semiconductors such as Si and Ge, electrons and holes usually form droplets,[6,7] with a fixed density inside the dropets that minimizes the energy per electron-hole pair.[4] For direct-band-gap semiconductors, it is believed that the lifetime of the photo-excited carriers is too short to allow spatial imhomogeneity and the formation of electron-hole liquid droplets. On the contrary, a uniform density throughout the illuminated region is always maintained and continuously changes when the pump intensity is varied. This is true even when a plasma is formed.[4] Therefore, for a given electron-hole pair density, the ground state of the system is either a uniform EMG or a uniform EHP. At zero temperature, the system will stay in the state with lower energy. However, for densities so high that the mean distance between carriers is smaller than the exciton Bohr radius, the state of well-separated excitons is not self-consistent anymore. The EHP becomes the only possible ground state under this circumstance. The density dependence of the ground-state energy per pair of the EHP has been studied extensively,[6,7] while the energy of each exciton (and thus the EMG) is fixed, except at very high densities. The binding energy of a free exciton is called the exciton Rydberg constant ($\mathcal{R}$). Photoluminesence and absorption experiments of bulk GaAs lead to the conclusion that the EMG persists up to the density where excitons start to overlap with one another. Beyond that density the EHP forms. This suggests that the energy of the EHP is never lower than that of the excitons. Theoretical prediction has been marginal[7] and will be discussed later. Clearly, any mechanism that reverses the relative energies of these two states and thus stabilizes the EHP as the ground state at lower densities will modify the nonlinear optical properties substantially. One of the potential candidates is the presence of a slowly varying electric potential modulation. It causes a long-range charge redistri-

bution for the EHP and lowers its energy, while the EMG is unaffected by the potential because it is composed of neutral particles. Indeed, our calculation shows that through the application of a sinusoidal electric field, the mean energy per electron-hole pair for the EHP can be lowered compared to that of the EMG, and the EHP becomes the ground state for e-h pair densities below a critical value n_c, which depends on the external potential. A transition between the EMG and the EHP occurs with a small change of density. The key point is that at such density, on the EMG side there is almost neither a PSF bleaching effect nor plasma screening for the exciton absorption peak due to the presence of other excitons, while on the EHP side the plasma screening is very effective because it is well above the Mott criterion $(5.4 \times 10^{14} \text{ cm}^{-3})$ for the bound e-h pair to exist.[8] The consequence is that the relaxation time of the (negative) photo-induced exciton absorption change is limited not by the lifetime of the carriers (still in the nanosecond range), but rather by the time the system takes to transform to its new ground state as the density decays through the critical value n_c. This transition time has been shown to be only a few picoseconds.[9]

In the following we shall first calculate the energies of the EHP including an external electric field and identify the critical densities n_c. Then we shall discuss the associated optical nonlinearities and the relaxation processes. Finally, we conclude with certain remarks on the limits of our calculations.

II. EHP ENERGY CALCULATION

The dimensionless parameter r_s is defined by $4\pi(a_B r_s)^3/3 \equiv 1/n$. For the exchange-correlation energy of the EHP, we use the universal behavior of Vashishta and Kalia.[7] The energy $\epsilon_{EMG}(r_s)$ of the EMG per pair is not always equal to the exciton Rydberg energy. There are at least two corrections to be taken into account: First, at low densities the formation of biexcitons will lower its energy;[10] second, at high densities, where the mean distance between the excitons is comparable to the exciton Bohr radius a_B, the interaction among the excitons will increase the energy. For the high-density correction of the EMG curve, we use the results of a hard-core Bose gas as a rough approximation.[11] The biexciton binding energy Δ is approximately equal to 0.5 meV.[12] Our discussion below, however, does not depend on the detailed behavior of $\epsilon_{EMG}(r_s)$. Then let us briefly review the theoretical results of the ground-state energies per pair of the EHP $\epsilon_{EHP}(r_s)$ without any electric field. For GaAs, unfortunately, the theoretically predicted minimal energy of EHP as a function of density is too close to the exciton Rydberg constant[13-15] and the question whether the EHP is ever the true ground state becomes difficult to answer. For semiconductors with larger $\mathcal{R}$ such as CdS and CuCl, the theoretical results, as shown in Fig. 1, are quite different from those for GaAs. The curves of the EMG and EHP do cross each other[16] when the external potential is zero. The crossing (at $r_s \simeq 1.9$ for CdS and $r_s \simeq 2$ for CuCl) of the EHP and EMG curves is also consistent with the experiments.[9]

To calculate the energy of the EHP under external potential, we use the standard density-functional theory (DFT). According to DFT, the ground-state energy is the minimum of a density functional (DF) $E[n_e(r), n_h(r)]$, where $n_e(r)$ and $n_h(r)$ are the electron and hole densities, respectively. The DF is usually written in the form[7]

$$E[n_e(r), n_h(r)] = E_{es} + E_k + E_{xc},$$

where the subscripts denote electrostatic, kinetic, and exchange-correlation energies, respectively. The exact form of E_{xc} is unknown. However, for a linear-response analysis, we need to know it only up to the second order in the fluctuations of the electron and hole densities around their mean value n, i.e., $m_e(r) \equiv n_e(r) - n$ and $m_h(r) \equiv n_h(r) - n$. Assuming a local DF, we have[7]

$$E[n + m_e(r), n + m_h(r)]$$

$$
\begin{aligned}
= E[n,n] &+ \frac{1}{2}\int \frac{e^2}{\kappa|r-r'|}[m_h(r) - m_e(r)] \\
&\times [m_h(r') - m_e(r')] d^3r\, d^3r' \\
&+ \frac{1}{2}\int [\epsilon_e^{(2)} m_e^2(r) + \epsilon_h^{(2)} m_h^2(r)] d^3r \\
&+ \sum_{i=e,h} \Lambda_i(n) \int |\nabla m_i(r)|^2 d^3r \\
&+ \sum_{i,j=e,h} \Gamma_{ij}(n) \int \nabla m_i(r) \cdot \nabla m_j(r) d^3r + O(m_e^4, m_h^4).
\end{aligned}
$$

$$(1)$$

Here κ is the background dielectric constant and e is the electron charge. The superscript (2) means the second derivative of $\epsilon_i n$ with respect to the density, evaluated at n_i. ϵ_e and ϵ_h are the electron and hole parts of the kinetic plus exchange-correlation energy per pair for a homogeneous system. The analytic form of the exchange-correlation energy used here is the universal form

$$\epsilon_{xc}(r_s) = \frac{A + Br_s}{C + Dr_s + r_s^2},$$

$$(2)$$

where A, B, C, and D are universal constants.[17] The expressions for $\Lambda_i(n)$ and $\Gamma_{ij}(n)$ can be found in Ref. 7. Since the terms of order m_i^3 vanish by inversion symmetry, the next lowest order is proportional to m_i^4. For convenience, we express the DF in terms of the Fourier transforms of the density fluctuations $\tilde{m}_e(k)$ and $\tilde{m}_h(k)$. Substituting

$$m_{e,h}(r) = \frac{1}{\sqrt{V}} \sum_k e^{ik \cdot r} \tilde{m}_{e,h}(k)$$

into Eq. (1), we have

$$E[n + m_e(r), n + m_h(r)]$$

$$= E[n,n] + \frac{1}{2}\sum_k [\tilde{m}_e(k)\tilde{m}_h(k)] M \begin{pmatrix} \tilde{m}_e(k) \\ \tilde{m}_h(k) \end{pmatrix}.$$
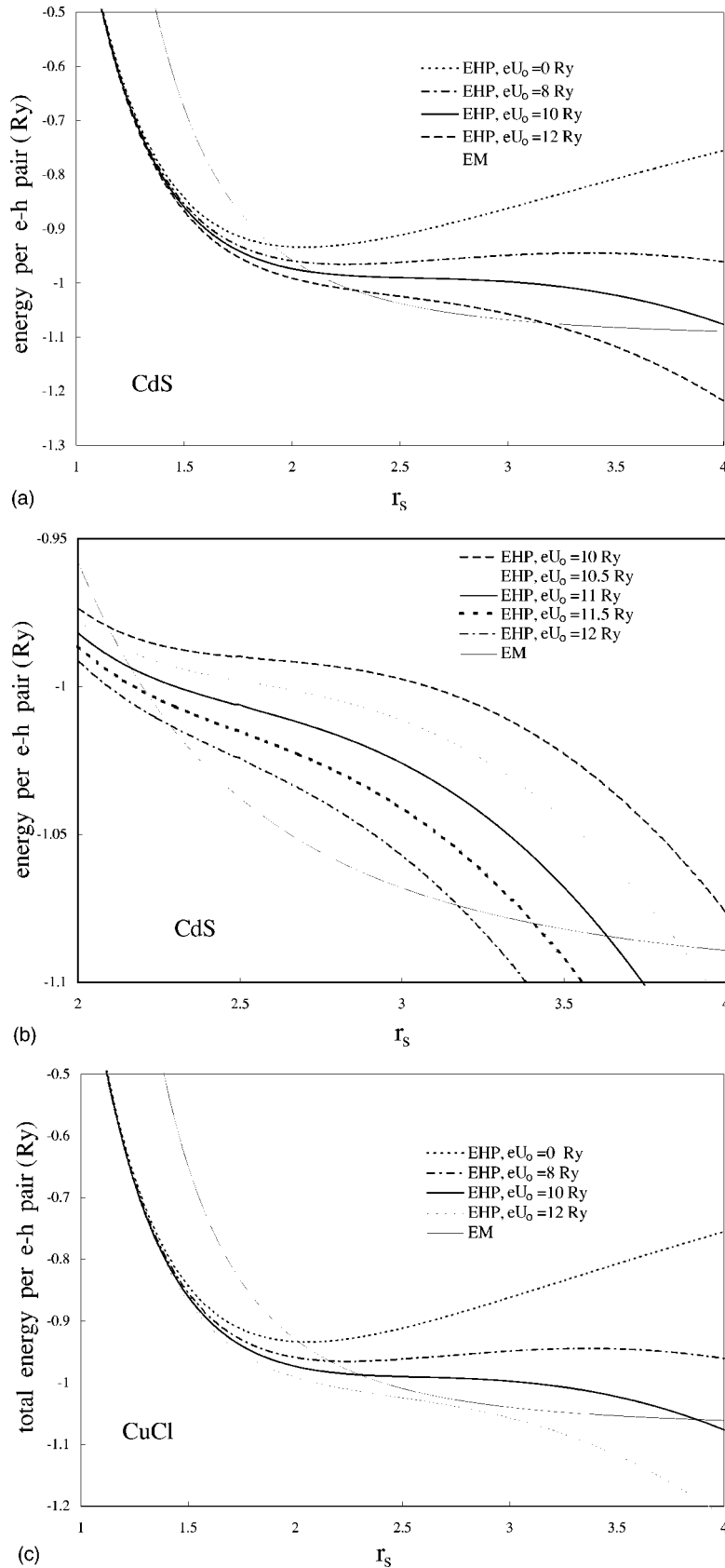
$$(3)$$

FIG. 1. Ground-state energies $\epsilon(r_s)$ per e-h pair of (a) and (b) CdS and (c) CuCl, under various external electric potentials, as functions of r_s. The EHP curves are obtained using the universal formula for the exchange-correlation energy [see Eq. (2)]. Since we approximate the excitons as neutral particles, the EMG curves are unchanged under the influence of external potential. The external potential is assumed to be sinusoidal with wavelength 1000 times of the exciton Bohr radius. The ground-state energy of the EHP can be reduced by the external potential and crosses the EMG curve at lower carrier density n_c. In (b) (for CdS) the evolution of n_c under the modulation of external potential is shown in detail. The result for CuCl is similar.

V is the system volume. The linear terms vanish due to the constraints $\int m_e(r)d^3r = \int m_h(r)d^3r = 0$. The 2×2 matrix M has the form

$$M = \begin{pmatrix} b & c \\ c & d \end{pmatrix},$$

with the matrix elements

$$b = \frac{4\pi e^2}{\kappa k^2} + \epsilon_e^{(2)} + k^2(\Lambda_e + \Gamma_{ee}),$$

$$c = -\frac{4\pi e^2}{\kappa k^2} + k^2\Gamma_{he},$$

$$d = \frac{4\pi e^2}{\kappa k^2} + \epsilon_h^{(2)} + k^2(\Lambda_h + \Gamma_{hh}). \tag{4}$$

Now we turn to the calculation of the ground-state energy of the EHP under an external potential $U(r)$. The new density functional E_U can be easily obtained by adding a new external potential energy term E_{ex} to the density functional E of the uniform system. In terms of density fluctuations, we have

$$E_U = E + E_{ex}, \quad E_{ex} = \sum_k e\tilde{U}(k)[\tilde{m}_h(k) - \tilde{m}_e(k)],$$

where $\tilde{U}(k)$ is the Fourier transform of the external potential $U(r)$. The density configuration that minimizes E_U can be obtained by the stationary conditions

$$\frac{\delta E_U}{\delta \tilde{m}_e} = \frac{\delta E_U}{\delta \tilde{m}_h} = 0, \tag{5}$$

which lead to the matrix equation

$$M\begin{pmatrix} \tilde{m}_e(k) \\ \tilde{m}_h(k) \end{pmatrix} = \begin{pmatrix} e\tilde{U}(k) \\ -e\tilde{U}(k) \end{pmatrix}. \tag{6}$$

Assuming $U(r) = U_0\cos(k_0 r)$, one can easily invert Eq. (6) and then substitute the solutions $\tilde{m}_e(k)$, $\tilde{m}_h(k)$ into E_U to obtain the energy $\epsilon_{EHP}(r_d)$.

In our calculation, the wavelength $2\pi/k_0$ of the external potential is chosen to be 1000 times the exciton Bohr radius. Such a $U(r)$ can be achieved, in principle, by a sinusoidal dopping profile. Other more practically feasible $U(r)$ should give qualitatively the same results, as long as a long-range charge redistribution is produced. The energy of the EMG is assumed to be unaffected by the external field because we are considering the long-wavelength limit, where the EMG's can be treated as pointlike neutral particles. One of the most interesting features is that when the external potential is strong enough, the ground-state energy of the EHP becomes substantially smaller than the EMG energy for a wide range of r_s.

Figure 1 shows the total energy per electron-hole pair under the influence of several external electric potentials for CdS [Figs. 1(a) and 1(b)] and CuCl [Fig. 1(c)]. In the inter-

val of $1 < r_s < 4$ plotted here, the relative density fluctuation $m_i(r_s)/n(r_s)$ can be estimated by

$$\frac{m_i(r_s)}{n(r_s)} \approx \frac{k_0^2 a_B^2}{12}\left(\frac{eU_0}{\mathcal{R}}\right)\left(\frac{\epsilon_i^{(2)}}{\epsilon_e^{(2)} + \epsilon_h^{(2)} + (\kappa k_0^2/4\pi e^2)\,\epsilon_e^{(2)}\epsilon_h^{(2)}}\right)r_s^3 \tag{7}$$

because the contributions from Λ_i, Γ_{ij} terms are very small. It turns out that the ratio is smaller than 0.01, so the linear-response approach is well justified. The empirical universal formula of $\epsilon_{xc}(r_s)$ used here is not expected to work for $r_s > 4$.[7,17] When the external potential is zero, the EMG state is more stable than the EHP state for r_s roughly larger than 2. As the external electric field is turned on, the energy of the EHP is reduced. The energy reduction is larger in the low e-h density (large r_s) region than in high density (small r_s) region. The reason is that the absolute charge-density fluctuation caused by a given external potential remains in the same order independently of the mean density n; therefore, the relative density fluctuation increases as r_s increases. When the external potential is not quite as large, there exists a critical density n_c (and a critical mean distance r_{sc}) such that the true ground state is the EMG for $n > n_c$ ($r_s < r_{sc}$) and the EHP for $n < n_c$ ($r_s > r_{sc}$). As U_0 increases continuously, r_{sc} becomes smaller and smaller. Finally, if the external potential is too large, r_{sc} ceases to exist, i.e., the EHP is more stable than the EMG in the whole r_s range within which the local DFT with universal $\epsilon_{xc}(r_s)$ applies. The material parameters used for our calculations can be found in Refs. 7 and 10.

III. OPTICAL NONLINEARITY

The anticipation of a mechanism for ultrafast nonlinear optics is now immediate. The critical value r_{sc} separates two different states: the EHP and the EMG. For $r_s > r_{sc}$ (EHP), the bleaching of the exciton absorption peak is due to the plasma screening of the Coulomb potential between the electrons and holes. On the other hand, for $r_s < r_{sc}$ (EMG), the bleaching is due to the PSF effect of the EMG. Since n_c is much above the Mott criterion for the existence of bound states, the bleaching of the exciton absorption in the EHP is nearly complete. On the other hand, the PSF is not expected to be significant for the same density of the EMG because the filling fraction is very small for $r_{sc} \gg 1$. Therefore, the exciton absorption peak is suddenly turned on or off when the density crosses n_c.

In order to get a more quantitative estimate of the nonlinearity, we consider finite-temperature situations, where the system becomes a statistical mixture of the EHP and EMG, with thermal distribution weights W_P and W_M, instead of a pure state of the EHP or EMG. W_P and W_M are assumed to satisfy the relation $W_P/W_M = e^{-\beta(\epsilon_{EHP} - \epsilon_{EMG})}$ and $W_P + W_M = 1$. $\beta = 1/k_BT$, where k_B is the Boltzmann constant and T the temperature. It is easy to see that $W_M(T,r_s) = (1 + \exp\{[\epsilon_{EMG}(r_s) - \epsilon_{EHP}(r_s)]/k_BT\})^{-1}$ and $W_P(T,r_s) = 1 - W_M(T,r_s)$. The effective probe absorption spectrum becomes

$$\alpha(\omega) = W_P\alpha_P(\omega) + W_M\alpha_M(\omega), \tag{8}$$
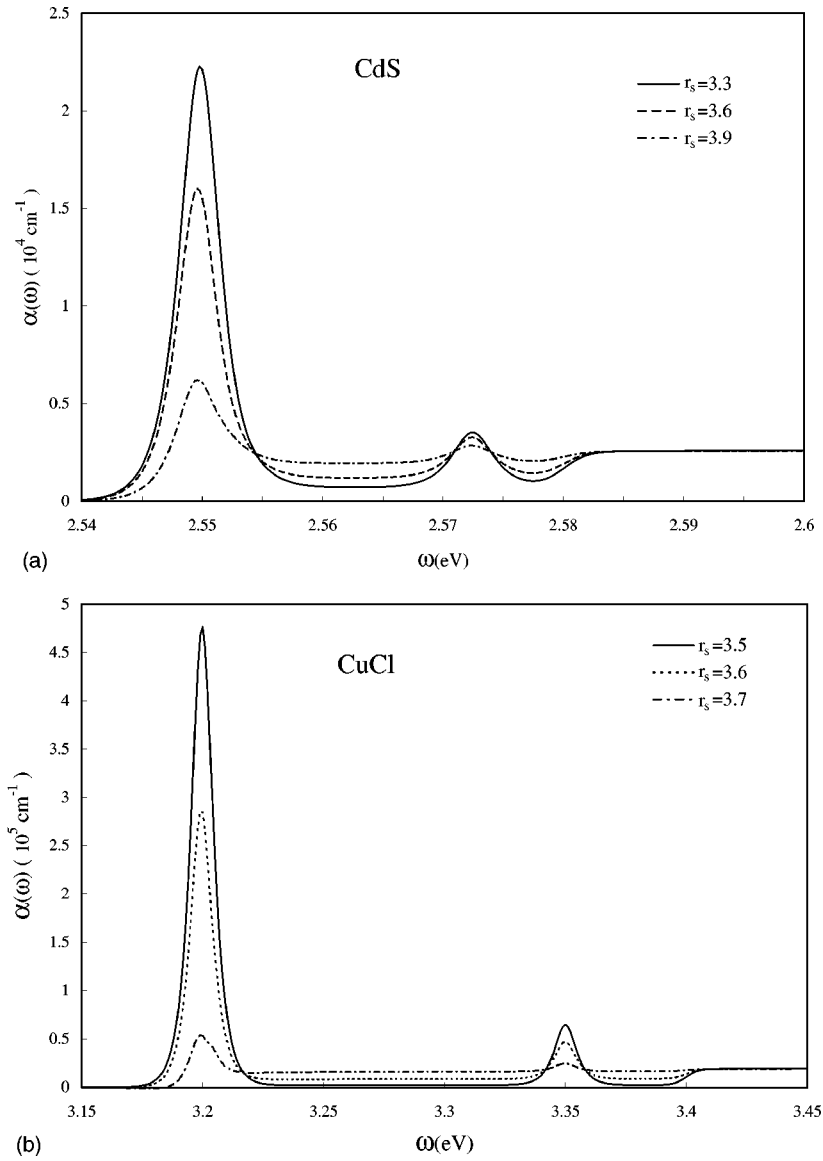
FIG. 2. Absorption spectra of (a) CdS and (b) CuCl under resonant pumping. The external potentials used here are $eU_0 = 11$ Ry for CdS and $eU_0 = 10.5$ Ry for CuCl and the temperature used for the thermal distributions is 10 K. For simplicity, only the first two exciton absorption peaks are kept to illustrate the nonlinear optical phenomena. U_0 is deliberately chosen so that the critical $r_{sc} = 3.6$ in both (a) and (b). As the carrier density decreases through n_c, the ground state changes from the EMG state into the EHP state and the bleaching of exciton absorption peaks is enhanced. The exciton absorption linewidths Γ are chosen to be 0.05 Ry for CdS and 0.02 Ry for CuCl.

where $\alpha_P(\omega)$ and $\alpha_M(\omega)$ are the probe absorption spectra in the presence of a pure EHP and EMG, respectively. We approximate $\alpha_M(\omega)$ by $(1 - r_s^{-3})\alpha_0(\omega)$. $\alpha_0(\omega)$ is the linear absorption spectrum of unexcited material[18] and the factor $1 - r_s^{-3}$ results from the PSF effect in the EMG state. For plasma absorption we have

$$\alpha_P(\omega) = \alpha_0 \tanh[\beta(\hbar\omega - E_g - \mu)/2]\frac{\hbar\omega}{\mathcal{R}}$$

$$\times \int_0^\infty dx \frac{\sinh[\pi g \sqrt{x}]}{\cosh[\pi g \sqrt{x}] - \cosh[\pi\sqrt{4g - xg^2}]}$$

$$\times \delta_\Gamma((\hbar\omega - E_g)/\mathcal{R} - x),$$

where $\mathcal{R}$, Γ, and g are the exciton Rydberg constant, absorption linewidth, and dimensionless screening length of the

Yukawa potential, respectively.[18] If the initial carrier density excited by the pump is much larger than the critical density n_{sc}, such that $\epsilon_{EHP} - \epsilon_{EMG} \gg k_B T$ and $W_M \gg W_P$, we have $\alpha(\omega) \simeq \alpha_0(\omega)(1 - r_s^{-3})$. The exciton absorption peak is sharp because $r_s \gg 1$. When the pump is suddenly turned off, the excited carrier density begins to go down through radiative recombinations and passes through n_{sc} sooner or later. During this period W_M decays rapidly to zero (W_P gets close to one) and finally the system becomes a mixture dominated by the EHP component. The exciton peak is then significantly suppressed due to the screening effect characteristic of the plasma state. Such a transition causes a striking change of the oscillator strength of the exciton absorption peak within a small range of carrier density.

The contrast of the exciton absorption peak between the two sides of the transition point is blurred at higher temperatures and sharpened at lower temperatures. Even though
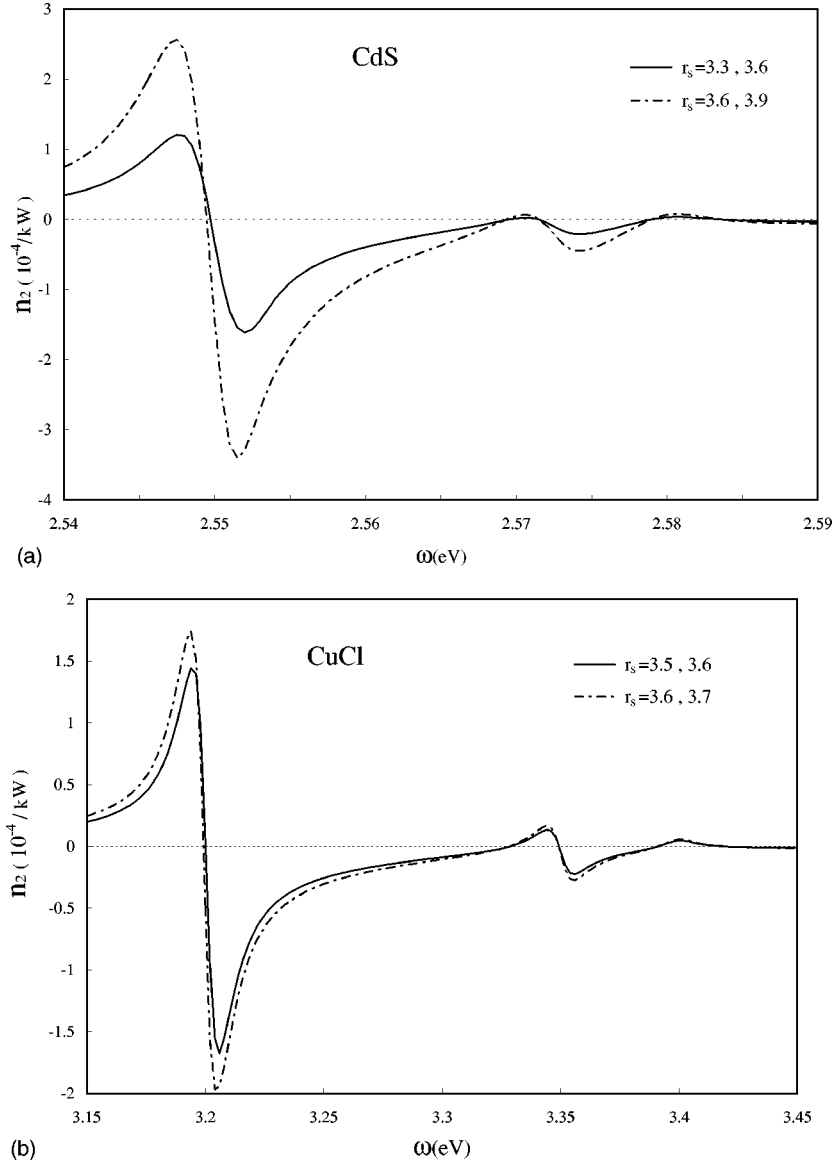
FIG. 3. Kerr effect of (a) CdS and (b) CuCl, calculated from the results of Fig. 2. In (a) the solid curve is the $n_2 \equiv \Delta n / \Delta I_p$ spectrum for CdS calculated from the difference in refractive index at two pump powers corresponding to $r_s = 3.3$ and 3.6. The dashed curve is for n_2 with $r_s = 3.6$ and 3.9. In (b) the solid curve is the n_2 spectrum for CuCl at two different carrier densities at $r_s = 3.5$ and 3.6 and the dashed curve is for $r_s = 3.6$ and 3.7. Remember that the critical $r_{sc} = 3.6$ in both (a) and (b).

GaAs is the most thoroughly studied direct-band-gap semiconductor, it is not a good material for observing the mechanism discussed above. The reason is that the exciton Rydberg constant in bulk GaAs is too small (4.2 meV) and so is $\epsilon_{EMG} - \epsilon_{EHP}$. Therefore, in order to get a significant change of W_P and W_M, the temperature must be very low (say $T < 1$ K). However, there exist other direct-band-gap semiconductors whose exciton Rydberg constant is much larger. We take CdS and CuCl as examples, in which both the exciton Rydberg constant and the ratios of the biexciton Rydberg constant over the exciton Rydberg constant are much larger than for GaAs.[19] Figure 2 shows the calculated results of the bleaching of the exciton absorption peak in these two materials. We can clearly see that as r_s increases through r_{sc}, the exciton absorption peak is reduced. Through the Kramer–Kronig relation, a corresponding change of the refractive index can be obtained from the absorption spectrum.

The corresponding nonlinear refractive index n_2, defined as the change of refractive index per kilowatt of pump power, is shown in Fig. 3. The e-h pair density n is related to the pump power I_p by $n = \alpha I_p \tau / \hbar \omega_p$, with absorption coefficient $\alpha \approx 10^5$ cm^{-1} and carrier relaxation time $\tau \approx 3.5$ ps for CuCl.[20] This nonlinear mechanism has an ultrafast decay time, which is equal to the time the EHP takes to cross the critical value r_{sc}, via radiative recombinations, and form the EMG. In fact, the transition time can be easily estimated from the energy curves $\epsilon_{EHP}(r_s)$ and $\epsilon_{EHP}(r_s)$. Through radiative recombination, the carrier density n decays exponentially: $n(t_0 + t)/n(t_0) = e^{-t/\tau}$. The crossover between the two states occurs in a density region (r_{sa}, r_{sb}) around r_{sc}. r_{sa} and r_{sb} are determined by the condition that the difference between ϵ_{EHP} and ϵ_{EMG} is equal to the thermal fluctuation energy $k_B T$. Around r_{sc} we can linearize $\epsilon_{EHP,EMG}(r_s)$ and obtain the relation

$$|G(r_{sb}-r_{sa})|=k_BT, \quad \text{with } G$$

$$=\left.\frac{d[\,\epsilon_{EHP}(r_s)-\epsilon_{EHP}(r_s)]}{dr_s}\right|_{r_{sc}}. \tag{9}$$

The size of the interval increases with the temperature. Consequently, the transition time $\tilde{t}$ for the system to go from r_{sa} to r_{sb} also increases with the temperature, as expected. It is straightforward to show that the relation between $\tilde{t}$ and the effective temperature T is

$$\tilde{t}=3\tau\ln\left(\frac{k_BT}{r_{sc}G}+1\right). \tag{10}$$

Using the energy curves in Fig. 2(b) for CuCl, $\tilde{t}$ is 1.9 ps when the effective plasma temperature T is 100 K and without an external potential. This result agrees well with the time-resolved photoluminescence experiments by Hulin et al.[20] In the presence of an external potential, the results depend in general on the strength of the potential eU_0 and the effective temperature T. For $eU_0=10.5$ eV and $T=100$ K, we get $\tilde{t}=3.06$ ps. For $T=10$ K, $\tilde{t}$ is reduced to only 0.3 ps. For other values of eU_0, $\tilde{t}$ is also of the order of picoseconds. Clearly, $\tilde{t}$ is the switching time of this mechanism of nonlinear optics.

IV. DISCUSSION

Some caution is needed in the calculational procedures we followed in this work. First, there exists an instability. The linear equation (6), which results from the stationary condition of the DF, will have no solution if the determinant of matrix M $\det(M)=bd-c^2$ becomes zero. In fact, $\det(M)$ does become zero for r_s equal to some instability value r_{si}, which is generally smaller than r_{sc}. This means that the charge-density fluctuation will diverge at such a particular carrier density no matter how small the external potential is. Actually, this instability continues to exist for all $r_s>r_{si}$ because one of the two eigenvalues of M becomes negative there. In other words, the spatially uniform e-h density distribution is not a minimum but a saddle point in the density-functional space. If we take this negative eigenvalue seriously, a spontaneous density inhomogeneity (breaking of translational invariance) will result and the electron-hole droplet would finally form. However, as mentioned in the Introduction, such an inhomogeneous true ground state is not realized in direct-band-gap material due to the lack of equilibration time. We therefore believe that the saddle-point solution is the physical state and nothing drastic is expected to happen around r_{si}. Interestingly, the singularity in the electron and hole density fluctuations does not cause a singularity in the total energy because the charge density n_h-n_e always remains finite. In fact, the singularity can be technically avoided by keeping the next-higher-order terms ($O(m_i^4)$) in the DF (1). Thus the stationary ansatz (5) leads to the nonlinear equation

$$M\begin{pmatrix}\tilde{m}_e(k)\\\tilde{m}_h(k)\end{pmatrix}+\frac{1}{2(2\pi)^3}\begin{pmatrix}\epsilon_e^{(4)}\tilde{m}_e(k)^3\\\epsilon_h^{(4)}\tilde{m}_h(k)^3\end{pmatrix}=\begin{pmatrix}e\tilde{U}(k)\\-e\tilde{U}(k)\end{pmatrix}. \tag{11}$$

Due to the third-order correction, the divergence problem is regulated and does not happen to the solutions of $\tilde{m}_i(k)$ anymore. The nonlinear correction to the previous linear solutions is found to be negligible, except near the divergence point r_{si}. It has practically no effect on the energy since it is already continuous. Therefore, all the results are almost the same as what we discussed in Sec. III and all the conclusions remain unchanged. Another limit of our calculation is that we do not know the behavior of $\epsilon_{EHP}(r_s)$ for $r_s>4$ because the exchange-correlation energy at low density is unknown. Nevertheless, in the extreme of $r_s\gg1$, $\epsilon_{EHP}(r_s)$ must approach eU_0, which is the energy difference between a dissociated electron and a hole far apart from each other. The general behavior of $\epsilon_{EHP}(r_s)$ under an external potential appears to be a very difficult problem. Fortunately, the transition point r_{sc} is within the range of validity of our approximations and the mechanism of nonlinear optics is unaffected by such limitations.

V. CONCLUSION

In conclusion, through the reduction of the ground-state energy of the EHP by an external potential, the critical density for the transition between EHP and EMG can be reduced by more than one order of magnitude. Based on the sharp contrast between the bleaching efficiencies of the EHP and EMG, a mechanism for nonlinear optics with a picosecond relaxation time is proposed. Because the effect is more pronounced at low temperatures, resonant pumping is required in order to produce cold excitons.

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*Electronic address: meng@cc.nctu.edu.tw

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