Ultrafast nonlinear optics due to electron–hole plasma in bulk semiconductors

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Abstract

It is theoretically demonstrated that, in the presence of an electric potential landscape, the ground-state energy of the electron–hole plasma can be substantially lowered against the ground-state energy of the excitons. The electron–hole plasma is found to be unstable at lower carrier densities. The critical carrier density for the transition between these two states can be reduced. This reduction provides a new mechanism of nonlinear optics for bulk direct band-gap semiconductors, with picosecond relaxation time, large nonlinearity, and requiring low pump intensity.

The mechanisms for intensity-dependent refractive index have been one of the most important subjects for the researches on nonlinear optics. As the application on all-optical switching is concerned, not only the nonlinearity, but also the relaxation time, are of primary importance. For resonant excitations, whose nonlinearity is usually due to the absorption changes induced by the photo-excited quasi-particles, one faces a trade-off between the above two factors. The relaxation is limited by the lifetime of the excited quasi-particles. However, any mechanism that reduces the lifetime will frequently lower the concentration of the quasi-particles for a given excitation intensity, and therefore diminish 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 quasi-particles usually sets the

ultimate limit for the switching time. In this paper, we present a new mechanism for resonant nonlinearity in bulk direct band-gap semiconductors under external electric potential. It does not suffer from the nonlinearity-relaxation time trade-off. This is because the relaxation time of this mechanism is not limited by the quasi-particle lifetime. Instead, it is only limited by the transition time between two different collective states, with distinct optical properties, of the quasi-particles. This transition time was found to be as small as a few picosecond. At the same time, the nonlinearity is enlarged.

First, take GaAs as an example. The nonlinear effect of bulk GaAs is appreciable only at very high excitation powers. For 3D materials, the principle mechanism for the exciton peak bleaching is the plasma screening effect. However, under resonant excitations, the electron–hole plasma (EHP) is formed only when the carrier density is as high

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as 10^{17} cm^{-3} [1,2], while the relaxation is limited by the nanosecond exciton lifetime [3]. For direct band-gap semiconductors, it is believed that the lifetime of the photo-excited carriers is too short to allow the formation of electron–hole liquid droplets. Instead, an uniform density is always maintained and continuously changed when the pump intensity is varied. This is true even when a plasma is formed [1]. Therefore, for a given electron–hole pair density, the ground state of the system is either an exciton molecule gas (EM), or an uniform EHP. At zero temperature, the system will stay in the state with lower energy, i.e., the ground state. The density dependence of ground state energy per pair of the EHP has been studied extensively [4, 5], while the energy of the EM is fixed except at very high densities. In particular, the energy is called the exciton Rydberg (Ry) for free excitons. As mentioned before, photoluminesence and absorption experiments lead to the conclusion that the EM persists up to densities around 10^{17} cm^{-3}, beyond which the mean distance among the excitons becomes smaller than the exciton Bohr radius a_B. Therefore the notion of excitons loses its meaning, and the EHP forms. This suggests that the energy of the EHP is never lower than that of the excitons. 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.

We demonstrate that through the application of a slowly varying electric potential landscape that causes a long-range charge redistribution for the EHP and lowers its energy, the energy of the EHP can be lowered against the EM. The EHP then becomes the ground state for pair densities above a critical value n_i, which is intrinsic to the material and is as low as 10^{16} cm^{-3}. Here i denotes instability (see below). When the density is even lower, the EHP becomes unstable and the system switches to EM. At such density, there is almost no phase-space filling (PSF) bleaching effect for the exciton absorption peak due to the presence of other excitons, while the plasma screening is still very effective, because it is still well above the Mott criterion (5.4×10^{14} cm^{-3}) [2, 6]. The consequence is that the relaxation time of the photo-induced absorption change is not limited by the lifetime of the carriers (still in the nanosecond range), but by the time the system takes to transform to its

new ground state, as the density decays through the critical value n_i. This time has been shown to be only a few picoseconds [7]. Besides GaAs, we will also discuss other semiconductors, e.g. CuCl, for which the energy of the EHP does becomes lower than that of the EM for densities higher than a critical value n_c, even without any external field.

Let us first briefly review the theoretical results on the ground-state energies of the EHP and EM without any electric field [5]. The ground-state energies per pair (in units of Ry), denoted by ε, of the EHP and EM as functions of the density are shown as the $ev_0/\text{Ry} = 0$ curve in Fig. 1. v_0, which measures the strength of the external potential, will be defined later. We use the dimensionless parameter r_s defined by $4\pi(a_B r_s)^3/3 \equiv 1/n$, instead of the real electron–hole pair density n. For the exchange-correlation energy of the EHP, we use the universal behavior of Vashishta and Kalia [5]. For the high-density correction of the EM curve, we use the results of a hard-core bose gas [8], with hard-core parameter chosen, quite phenomenologically and roughly, to be 20 Å. Our following discussions, however, do not depend on the detailed behavior of the $\varepsilon(r_s)$ for the EM. A shift of Δ below the Rydberg for the EM ground-state energy is due to the binding energy of biexciton, and bound exciton. These curves are consistent with the experiments that the EHP forms only when the density is higher than 10^{17} cm^{-3} ($r_s < 1$). For CuCl, the theoretical results [9], as shown in Fig. 2 ($ev_0/\text{Ry} = 0$ curve), are quite different. In particular, the EHP and EM curves cross each other, which is also consistent with the experiments [7].

To calculate the energy of the EHP under external potential, we use the density functional theory (DFT). As mentioned before, an uniform EHP is stable against small density fluctuations only when the mean electron–hole pair density n is above certain value n_i. We first demonstrate it by a stability analysis, then calculate, for $n > n_i$, the effect of external potential on the ground-state energy to the lowest order.

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 [5]

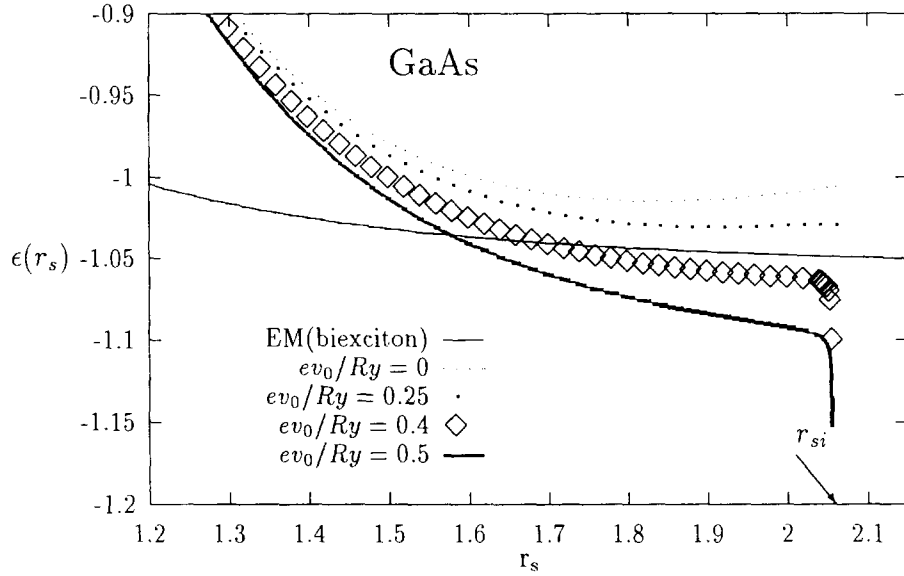$$E[n_e(r), n_h(r)] = E_{es} + E_k + E_{xc},$$

Fig. 1. The EHP ground-state energy $\varepsilon(r_s)$ of GaAs for various v_0's are shown, together with the EM (biexciton) energy, which is independent of v_0. The sharp drop of $\varepsilon(r_s)$ as r_s approaches r_{si} is due to the fact that one of the eigenvalues of M approaches zero, and the linear response of the system to the external field diverges. One sees that as $ev_0/Ry > 0.4$, the ground state becomes the EHP for $r_s < r_{si}$, while the ground state remains the EM for $r_s > r_{si}$ for any v_0. Δ is taken to be 0.06Ry [3].
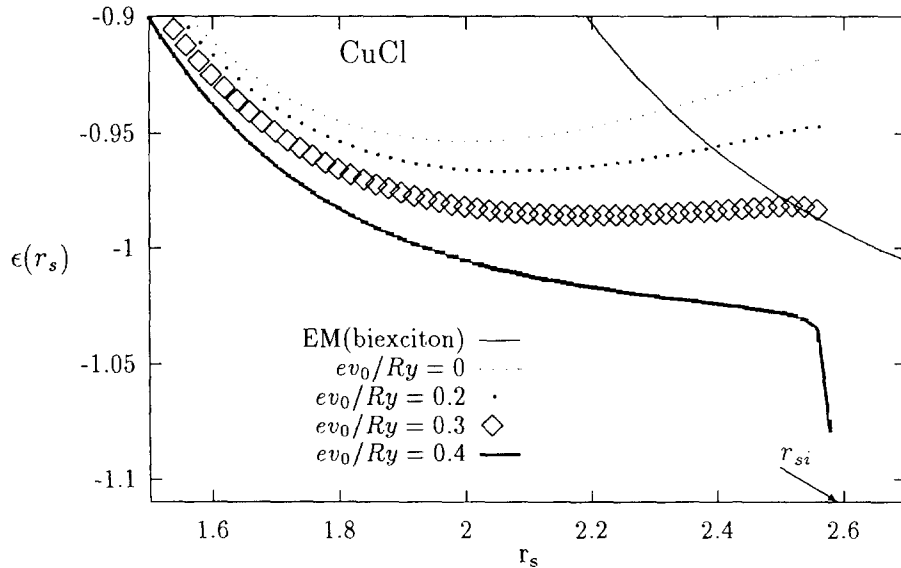

Fig. 2. Similarly to Fig. 1, the ground-state energy of the EHP for CuCl are shown for various v_0's. For $ev_0/Ry < 0.3$, the transition r_s between the EHP and EM increases with ev_0. For $ev_0/Ry > 0.3$, the transition happens at r_{si} ($\simeq 2.59$). See text for the associated nonlinear optical effects. Δ is taken to be 0.08Ry [11].

where the subscripts denote electrostatic, kinetic and exchange-correlation energies, respectively. The exact form of E_{xc} is unknown. However, for the purpose of stability 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 [5]

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

Here κ is the background dielectric constant and e is the electron charge. ε_e and ε_h are the electron and hole parts of the kinetic and exchange-correlation energy per pair for a homogeneous system. The superscript "(2)" means the second derivative with respect to the densities, evaluated at n. The expressions for $\Lambda_i(n)$ and $\Gamma_{ij}(n)$ can be found in Ref. [5]. For convenience, we express the DF in terms of the Fourier transforms of their density fluctuations $\tilde{m}_e(k)$ and $\tilde{m}_h(k)$. Substituting

$$
\tilde{m}_{e,h}(k) = \frac{1}{\sqrt{V}} \int e^{-ik \cdot r} m_{e,h}(r) \, \mathrm{d}^3r,
$$

with V being the system volume, into Eq. (1), we have

$$
\begin{aligned}
E[n &+ m_e(r), n + m_h(r)] \\
&= E[n,n] + \frac{1}{2} \sum_k (\tilde{m}_e(k) \tilde{m}_h(k)) M \begin{pmatrix} \tilde{m}_e(k) \\ \tilde{m}_h(k) \end{pmatrix}.
\end{aligned}
\tag{2}
$$

The linear terms vanish due to the constraints $\int m_e(r) \, \mathrm{d}^3r = \int m_h(r) \, \mathrm{d}^3r = 0$. The two by two matrix M has the form

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

with the matrix elements

$$
\begin{aligned}
b &= \frac{4\pi e^2}{\kappa k^2} + \varepsilon_e^{(2)} + k^2(\Lambda_e + \Gamma_{ee}), \\
c &= -\frac{4\pi e^2}{\kappa k^2} + k^2 \Gamma_{he}, \\
d &= \frac{4\pi e^2}{\kappa k^2} + \varepsilon_h^{(2)} + k^2(\Lambda_h + \Gamma_{hh}).
\end{aligned}
\tag{3}
$$

The uniform electron and hole densities minimize the DF if and only if both of the eigenvalues of M are positive. It turns out that this is true only when n is larger than a critical value n_i, or when r_s is smaller the corresponding critical value r_{si}. At the critical density, the determinant of M is zero. The behaviors of the eigenvalues and the determinant, as functions of r_s, are shown in Fig. 3. For $r_s > r_{si}$, the EHP is not stable. EM is expected to be the only possible state of the system.

Now we turn to the calculation of the ground-state energy of EHP under external potential $V(r)$, with the condition $r_s < r_{si}$, where both EHP and EM are possible. The new density functional E_V 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

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

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

$$
\frac{\delta E_V}{\delta \tilde{m}_e} = \frac{\delta E_V}{\delta \tilde{m}_h} = 0,
\tag{4}
$$

which leads to the matrix equation

$$
M \begin{pmatrix} \tilde{m}_e(k) \\ \tilde{m}_h(k) \end{pmatrix} = \begin{pmatrix} -e\tilde{V}(k) \\ e\tilde{V}(k) \end{pmatrix}.
\tag{5}
$$

Assuming $V(r)$ is equal to $v_0 \cos(k_0 r)$, one can easily evaluate the ground-state energy per pair ε to the order of $(v_0)^2$. The r_s dependances of ε for several v_0's are plotted in Fig. 1. In our calculation, the wave length $2\pi/k_0$ of the external potential is to be 100 times of the exciton Bohr radius. Such $V(r)$ can be achieved, in principle, by a sinusoidal doping modulation, with equal total number of donors and accepters. Other more practically feasible $V(r)$ should give qualitatively the same results, as long as a long-range charge
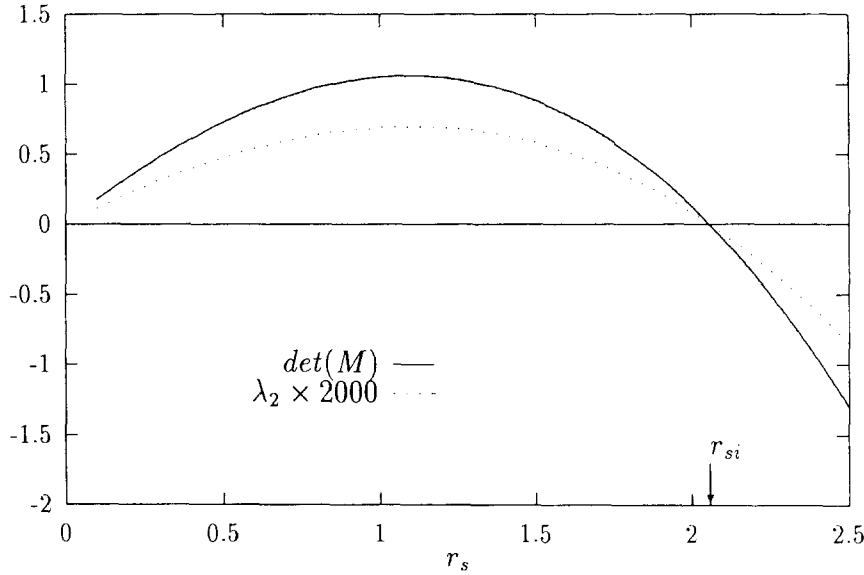
Fig. 3. The determinant (det(M)), and one of the two eigenvalues (λ_2), of the matrix M are plotted as functions of r_s. Another eigenvalue λ_1 stays basically a positive constant in this range of r_s. When $r_s > r_{si}$ ($\simeq 2.06$), λ_2 (and det(M)) becomes negative, and the uniform EHP is not stable. The values of det(M) are in units of $(4\pi a_B^3 \text{Ry}/3)(4\pi e^2/\kappa k_0^2)$, and λ_2 in units of $4\pi a_B^3 \text{Ry}$.

redistribution is produced. In fact, our result is similar to the calculation for fast varying potentials [10]. The energy of the EM is assumed to be unaffected by the external field, because we are considering the long-wavelength limit, where the EM's can be treated as point-like neutral particles. One of the most interesting features is that when the external potential is strong enough, the ground-state energy of the EHP can be substantially smaller than the EM energy for a wide range of r_s below r_{si}. The divergency at r_{si} is due to the ignorance of all higher-order terms of the density fluctuations in Eq. (5). The reason is as follows. If we include the fourth-order terms of the density fluctuations m_e and m_h in Eq. (1) (no third-order terms due to inversion symmetry), there will be terms proportional to the third power of $\tilde{m}_e$ and $\tilde{m}_h$ with finite coefficients on the left-hand side of Eq. (5), in addition to the linear term. Therefore, even when the determinant of M vanishes, the density fluctuations will not diverge. Instead, they will be proportional to the one-third of the external potential V. However, the inclusion of the higher-order terms does not change the order between the EHP and EM energies. It only removes the divergency near $r_s = r_{si}$ in Fig. 1. In fact, the

linear response results are expected to be very accurate except at the immediate neighborhood of r_{si}, because the relative density fluctuation is very small (0.1%) for the external potentials considered here. Therefore, as long as nonlinear optics mechanism is concerned, linear response calculation is enough.

The anticipation of a mechanism for ultrafast nonlinear optics is now immediate. For GaAs, the critical value r_{si} separates two different states: EHP and EM. For $r_s < r_{si}$, 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 $r_s > r_{si}$, the bleaching is due to the PSF effect of the EM. Since r_{si} is much larger than one, while n_i is much above the Mott criterion, it is expected that the bleaching of the EHP is significantly more efficient than that of the EM [2]. In fact, under resonant pumping, when the carrier density is above the critical value n_i, an EHP will be formed, and the exciton peak in the absorption spectrum will be completely bleached, while below n_i, the exciton absorption peak remains basically unbleached (see Fig. 4). This nonlinear mechanism has an ultrafast decay time, which is equal to the time the EHP takes to cross the critical
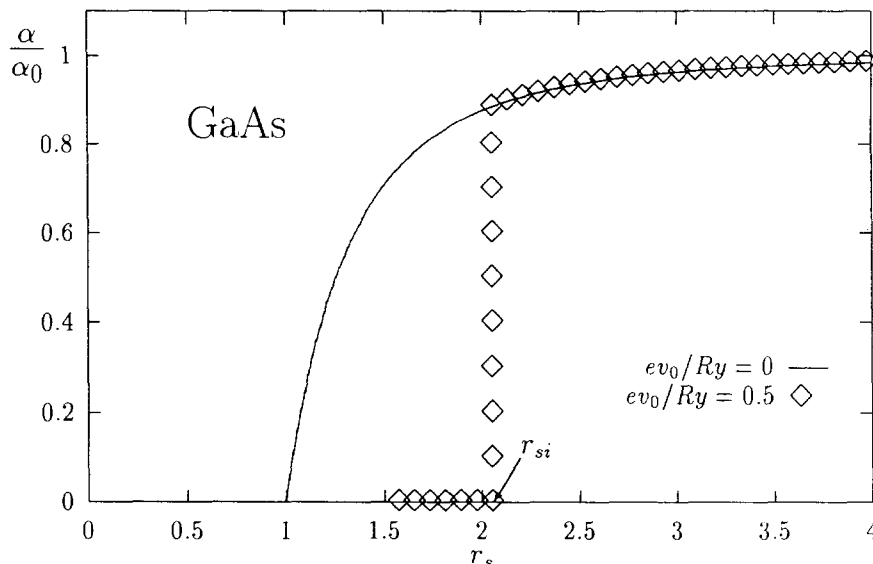
Fig. 4. The exciton bleaching factor α/α_0 are shown for two cases: $ev_0/Ry = 0$ and $ev_0/Ry = 0.5$. $\alpha(r_s)$ is the absorption coefficient at the 1s exciton resonance when the pair density parameter is r_s, and α_0 is the absorption coefficient at the low excitation limit. For $ev_0/Ry = 0$, we have EHP when $r_s < 1$ and EM when $r_s > 1$. The gradual increase of α is due to the decrease of PSF effect. For $ev_0/Ry = 0.5$, we have EHP when $r_s < r_{si}$ and EM when $r_s > r_{si}$. The sharp increase of α is due to the sudden disappearance of the plasms screening effect. The bleaching of the EHP is assumed to be perfect, while the bleaching due to excitons is approximated as the $1 - r_s^{-3}$. Note that r_s^{-3} is the volume (and the phase space) fraction occupied by the existing excitons.

value r_{si}, via radiative recombinations, to form EM. It is found that, for uniform EHP, this time of the order of a few picoseconds [7]. In the presence of the external potentials considered here, the relative change in the carrier densities is only about 0.1% except at the immediate neighborhood of r_{si}, as mentioned above. Therefore, the recombination process and the transition time are believed to remain the same as the uniform EHP. After the transition, a full exciton peak for the absorption will recover. Through the Kramer–Kronig relation, a corresponding change of the refractive index will also occur.

For the case of CuCl, there is a transition between EHP and EM happening at quite a high density ($n \simeq 10^{20}\,\mathrm{cm}^{-3}$ [7], $r_s \simeq 2.9$). The effect of the external potential is to reduce this transition density n_c (with r_c the corresponding dimensionless parameter) continuously, when v_0 is nonzero but small. When v_0 is further increased, the energy of the EHP for all $r_s < r_{si}$ becomes lower than the EM. r_{si} then takes over r_c and becomes the transition point between these two states, like the case of GaAs. Therefore, the con-

trast of the exciton absorption peak between the two sides of the transition can be magnified, and the nonlinearity enhanced. Basic features are summarized in Fig. 2.

In conclusion, using linear response LDA calculations, we show that through the modulation of the ground-state energy of the EHP by an external potential, the EHP becomes the ground state of GaAs, except for low densities where an intrinsic instability occurs. For CuCl, the critical density for the transition between EHP and EM can be reduced by the external potential. Based on the sharp contrast between the bleaching efficiencies of the EHP and low-density EM, a scheme for nonlinear optics, with picosecond decay time, is proposed. Because only the ground-state energy is discussed, in order to observe this effect, resonant pumping is required to produce cold excitons.

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