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2003 J. Phys.: Condens. Matter 15 3813

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Analytic Franz–Keldysh effect in one-dimensional polar semiconductors

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Received 16 January 2003, in final form 2 April 2003

Published 23 May 2003

Online at stacks.iop.org/JPhysCM/15/3813

Abstract

The optical properties of a one-dimensional polar semiconductor in a strong electric field are considered. This class of materials includes non-centrosymmetric III–V inorganic quantum wires but also polar conjugated polymers such as polymethineimine. The polar Franz–Keldysh effect is derived via an analytic expression for the complex dielectric constant including line broadening and linear field terms. Results for the high-field non-perturbative regime as well as the low-field expansion are presented.

1. Introduction

The Franz–Keldysh effect [1, 2] is a classic example of a non-perturbative phenomenon in solid-state physics. It describes the influence of a strong electric field on the optical properties of a semiconductor. The well-known signatures of the Franz–Keldysh effect are field-induced absorption below the band gap and an oscillatory modulation of the spectrum above the gap. Following the pioneering calculations of Franz and Keldysh for the absorption edge, several authors managed to derive analytical expressions covering the entire optical spectrum. Callaway [3] and Tharmalingam [4] obtained very elegant and compact expressions for the optical constants in terms of Airy functions. These authors considered bulk two-band semiconductors with isotropic effective masses. Subsequently, Aspnes [5, 6] generalized these results to cover anisotropic effective masses as well. To complete the picture, closed-form expressions for low-dimensional structures have been derived. Hence, two-dimensional semiconductors were considered by Aymerich and Bassani [7] and, very recently, the one-dimensional case covering materials such as quantum wires and conjugated polymers was treated by the present authors [8].

A major virtue of this impressive body of work lies in the successful derivation of closed-form analytic formulae for a highly non-perturbative phenomenon. In fact, the essential aspects of the Franz–Keldysh effect are absent in any finite-order perturbation calculation. This is clear from the exponential and oscillatory (trigonometric) dependence on the field strength. In addition, closed-form expressions provide simple relations for the dependence

on, for example, material parameters, and may readily be compared with experimental results. Their elegance and compactness are only obtained at a certain cost, however: (1) the neglect of exciton effects and (2) the adoption of the effective mass approximation (EMA). The electron–hole interaction responsible for the formation of excitons has a potentially large influence on the electro-optic spectra. The absorption lines of localized exciton states are essentially just Stark shifted in the presence of the applied field. In contrast, the oscillator strength of continuum resonances is completely redistributed. The significance of electron–hole interaction is determined by the exciton binding energy. Thus, the enhanced binding energy of excitons in low-dimensional structures [9] testifies to the importance of electron–hole interaction in these structures. Regarding the EMA, the situation is somewhat different. Though rarely emphasized, this approximation enters at two levels. First, there is the obvious neglect of non-parabolicity in the dispersion of transition energies throughout the Brillouin zone. Secondly, in the absence of a periodic potential the Bloch part of the wavefunction is missing. Hence, the \vec{k} -vector dependence of the optical transition matrix element is necessarily approximated or even neglected altogether. The neglect of non-parabolicity is expected to be reasonable for a direct-gap semiconductor in the vicinity of the energy gap. Similarly, the \vec{k} -dependence of Bloch-function momentum matrix elements is expected to be weak (quadratic) near the gap except in one special situation: that of a polar semiconductor. In this particular case, the k -dependence has a linear term, which in turn leads to a linear (Pockels) electro-optic effect. Polar semiconductors are of great practical importance as electro-optic modulators operating in the low-field regime [10]. The quadratic (Kerr) electro-optic effect of a non-polar or centrosymmetric semiconductor is much weaker in a low or moderate field and, thus, less suited for device applications.

The purpose of the present paper is to extend our previous work [8] on one-dimensional non-polar semiconductors to polar ones. In the non-polar case, analytic Franz–Keldysh type expressions for both real and imaginary parts of the optical spectrum including the presence of line broadening were derived within the EMA and the free-carrier limit. Extension to the exciton case was achieved by numerical diagonalization of the electron–hole pair eigenvalue problem. In the present work we wish to expand the analytical approach as far as possible and, hence, electron–hole interaction will be left for future work. A rigorous inclusion of linear as well as higher odd-order field terms will be presented, however. Analytic results for the complex dielectric function including line broadening are presented in terms of Airy functions. The significance of the new terms is discussed in low- as well as high-field cases. Thus, the present work is a significant improvement towards the goal of obtaining analytical results for the Franz–Keldysh effect in real one-dimensional materials. Our results immediately apply to the electro-optic properties of non-centrosymmetric (e.g. GaAs) quantum wires and polar conjugated polymers such as polymethineimine [11].

2. Theoretical model

Throughout, we stay within a two-band model with a completely filled valence (v) band and empty conduction (c) band. The starting point for the analysis is the momentum matrix element between these bands. Neglecting the intra-atomic contribution [12], which is appropriate for materials having strong interatomic coupling, the matrix element in a tight-binding representation is given by

$$p_{vc}(k) = \frac{m_0}{\hbar} \langle v | \frac{\partial H}{\partial k} | c \rangle = -i \frac{m_0}{\hbar} E_{cv}(k) z_{vc}(k), \quad (1)$$

where m_0 is the free electron mass and $z_{vc}(k)$ is the matrix element of the interatomic position operator $\hat{z} \equiv i \frac{\partial}{\partial k}$. The latter equality in equation (1) is easily derived from the

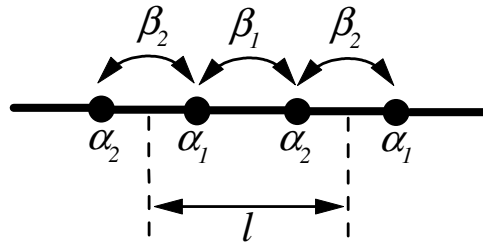


Figure 1. Linear ‘super-alternating’ chain with alternating on-site energy integrals α_1 and α_2 and hopping integrals β_1 and β_2 . The linear extension of the unit cell is l .

relation $\frac{\partial}{\partial k} \langle v|H|c \rangle = 0$. Next, we expand the matrix element in the vicinity of the band gap. For notational simplicity, we take the gap to lie at $k = 0$, but any other position could equally well be applied. The transition energy $E_{cv}(k)$ has no linear variation near the energy gap $E_g = E_{cv}(0)$. The variation of the position matrix element, however, is given by $i \frac{\partial}{\partial k} z_{vc}(k) = i \{ \frac{\partial}{\partial k} \langle v|\hat{z}|c \rangle + \langle v|\hat{z}^2|c \rangle$. Hence, by applying the closure theorem to the first term it follows that $p_{vc}(k) \approx p_{vc} \{ 1 + ikl_P \}$, where $p_{vc} \equiv p_{vc}(0)$ is the usual zone centre value and

$$l_P = z_{vv} + z_{cc} - (z^2)_{vc}/z_{vc} \quad (2)$$

is a characteristic *polarity* length related to the conduction and valence band dipole moments and the quadrupole transition matrix element. It is independent of the choice of origin. As an example, consider the simple chain in figure 1. For such a chain with alternating on-site energy integrals α_1 and α_2 and alternating hopping integrals β_1 and β_2 , one finds [13]

$$l_P = \frac{l(\alpha_1 - \alpha_2)\beta_1\beta_2}{(\beta_2^2 - \beta_1^2)[(\beta_2 - \beta_1)^2 + (\alpha_1 - \alpha_2)^2]^{1/2}}, \quad (3)$$

where l is the length of the unit cell. In this particular case, where $p_{vc}(k)$ can be calculated exactly [13], the general relation $p_{vc}(k) \approx p_{vc} \{ 1 + ikl_P \}$ is readily verified from an expansion of the full expression. This ‘super-alternating’ chain represents, in fact, the π bands in polymethineimine, in which the two sites of the unit cell are C and N atoms respectively, and Peierls dimerization is responsible for the bond alternation $\beta_1 \neq \beta_2$. The result in equation (3) shows that the polarity length l_P is of the order of the unit cell dimension for polymethineimine. Notice that when $\alpha_1 = \alpha_2$ the model describes polyacetylene (with C on both sites in the unit cell), which is centrosymmetric. Hence, no linear term can exist and, indeed, equation (3) vanishes in this limit. Note, also, that equation (3) has been derived under the condition that $\beta_1 \neq \beta_2$. For a non-dimerized chain with $\beta_1 = \beta_2$ it is readily shown that the momentum matrix element is of the form $p_{vc}(k) = ak + bk^3 + O[k^5]$. Since odd and even powers of k are not mixed in this case, the linear electro-optic contribution vanishes as expected because a non-dimerized chain is clearly centrosymmetric.

For a simple material such as polymethineimine the polarity length can be obtained analytically. However, even for more complicated compounds such as GaAs or other zinc-blende semiconductors, the polarity length is easily obtained numerically from the wavelength dependence of the momentum matrix element. As an example, we consider a GaAs wire grown along the [111] direction. Near the band gap the transition between light-hole and lowest conduction band is entirely dominant and in order to describe the wavelength dependence of the accompanying momentum matrix element we adopt the empirical pseudopotential method [14]. Hence, we calculate the matrix element between cell-periodic Bloch functions using the bulk

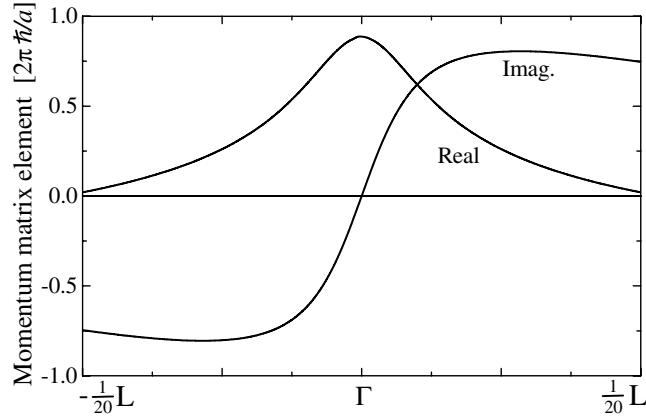


Figure 2. Real and imaginary parts of the momentum matrix element along the $\Gamma \rightarrow L$ direction for the transition between light-hole and lowest conduction band of GaAs.

band states. This simplification corresponds to applying the envelope-function approximation, for which the Bloch part of the quantum wire wavefunction is assumed identical to the bulk Bloch function. In figure 2, the matrix element along the $\Gamma \rightarrow L$ direction is shown in units of $2\pi\hbar/a$, with a the lattice constant. Near Γ the result can once again be fitted to the form $p_{vc}(k) \approx p_{vc}\{1 + ikl_P\}$, but here $l_P \approx 15a$, which is not surprising considering the highly polar character of zinc-blende semiconductors along the [111] direction. Thus, a substantial electro-optic effect is expected for these materials in agreement with experiments [10].

3. Electric field effects

In the presence of an applied electric field, k is no longer a good quantum number. Rather, the envelope function of the α band state ($\alpha = v, c$) is a plane-wave superposition with weight $\varphi_\alpha(k)$ given by the Fourier transform of an Airy function [15]. Hence, the full momentum matrix element $\langle \psi_v | \hat{p} | \psi_c \rangle$ is equal to

$$\begin{aligned} \langle \psi_v | \hat{p} | \psi_c \rangle &= \int_{-\infty}^{\infty} p_{vc}(k) \varphi_v^*(k) \varphi_c(k) dk \\ &\approx p_{vc} \int_{-\infty}^{\infty} \{1 + ikl_P\} \varphi_v^*(k) \varphi_c(k) dk. \end{aligned} \quad (4)$$

In the notation of [8], the k -integration leads to [15]

$$\langle \psi_v | \hat{p} | \psi_c \rangle = \frac{p_{vc}}{E_f} \left\{ \text{Ai} \left(\frac{E_g - E_{cv}}{E_f} \right) + l_P f^{1/3} \text{Ai}' \left(\frac{E_g - E_{cv}}{E_f} \right) \right\}, \quad (5)$$

where E_{cv} is the transition energy in the presence of the field and $E_f = \hbar^2 f^{2/3} / (2\mu)$ is the field energy with $f = 2\mu eF / \hbar^2$, μ being the reduced mass. To first order in the polarity length it is now straightforward to demonstrate that the imaginary part of the unbroadened dielectric constant (cf equation (7) of [8]) is given by

$$\tilde{\epsilon}''(\omega) = \frac{\tilde{C}}{(\hbar\omega)^2 E_f^{1/2}} \left\{ \text{Ai}^2 \left(\frac{E_g - \hbar\omega}{E_f} \right) + 2l_P f^{1/3} \text{Ai}' \left(\frac{E_g - \hbar\omega}{E_f} \right) \text{Ai} \left(\frac{E_g - \hbar\omega}{E_f} \right) \right\}. \quad (6)$$

For clarity, we have introduced a ‘tilde’ in order distinguish the present result from the original expression of [8], which is valid for non-polar materials only. In the expression

above, \tilde{C} is a material-dependent constant equal to $2^{3/2}\pi\hbar e^2\mu^{1/2}|p_{vc}|^2/(\varepsilon_0 m_0^2 A)$, where ε_0 is the vacuum permittivity and A is the cross section of the semiconductor. Unfortunately, the unbroadened result in equation (6) is only of minor physical importance since the limit $F \rightarrow 0$ of the spectrum displays increasingly rapid oscillations and is divergent at the band gap. Hence, to incorporate broadening (and compute the real part of the spectrum as well) a rather cumbersome convolution integral is required [8]. A substantial simplification is gained, however, by applying the following mathematical trick. First, it is noticed that equation (6) can be rewritten as

$$\tilde{\varepsilon}''(\omega) = \left\{ 1 + el_P F \frac{\partial}{\partial E_g} \right\} \varepsilon''(\omega), \quad (7)$$

where $\varepsilon''(\omega)$ is the result for non-polar materials given by equation (6) with $l_P = 0$. In order to obtain equation (7), the relation $f^{1/3} E_f = eF$ has been applied. Secondly, the convolution has already been applied to $\varepsilon''(\omega)$ in [8] and leads to a complex dielectric constant $\varepsilon_\Gamma(\omega)$. Hence, it follows directly that the complex dielectric constant $\tilde{\varepsilon}_\Gamma(\omega)$ including linear field terms is related to the non-polar result $\varepsilon_\Gamma(\omega)$ via

$$\tilde{\varepsilon}_\Gamma(\omega) = \left\{ 1 + el_P F \frac{\partial}{\partial E_g} \right\} \varepsilon_\Gamma(\omega). \quad (8)$$

If, for the sake of brevity, only the resonant part is retained the final expression reads as

$$\begin{aligned} \tilde{\varepsilon}_\Gamma(\omega) \approx 1 + \frac{\tilde{C}}{(\hbar\tilde{\omega})^2 E_f^{1/2}} \left\{ \text{Ai Bi} \left(\frac{E_g - \hbar\tilde{\omega}}{E_f} \right) + i \text{Ai}^2 \left(\frac{E_g - \hbar\tilde{\omega}}{E_f} \right) \right\} \\ + \frac{el_P F \tilde{C}}{(\hbar\tilde{\omega})^2 E_f^{3/2}} \left\{ (\text{Ai Bi})' \left(\frac{E_g - \hbar\tilde{\omega}}{E_f} \right) + 2i \text{Ai Ai}' \left(\frac{E_g - \hbar\tilde{\omega}}{E_f} \right) \right\}. \end{aligned} \quad (9)$$

This expression extends our analytic treatment of the Franz–Keldysh effect to polar semiconductors. It is the main result of the present paper. Several shorthand notations are introduced in the expression above: $\tilde{\omega} = \omega + i\Gamma$ is the complex frequency including broadening and we use $\text{Ai Bi}(x) \equiv \text{Ai}(x) \text{Bi}(x)$, $(\text{Ai Bi})'(x) \equiv \text{Ai}(x) \text{Bi}'(x) + \text{Ai}'(x) \text{Bi}(x)$ and finally $\text{Ai Ai}'(x) \equiv \text{Ai}(x) \text{Ai}'(x)$. If we introduce the expansion $\tilde{\varepsilon}_\Gamma = 1 + \chi^{(1)} + \chi^{(2)} F + \chi^{(3)} F^2 + \dots$, the different orders are readily identified as

$$\chi^{(1)}(\omega) = \frac{\tilde{C}}{2\pi(\hbar\tilde{\omega})^2(E_g - \hbar\tilde{\omega})^{1/2}} \quad (10)$$

$$\chi^{(2)}(\omega) = -\frac{\tilde{C}el_P}{4\pi(\hbar\tilde{\omega})^2(E_g - \hbar\tilde{\omega})^{3/2}} \quad (11)$$

$$\chi^{(3)}(\omega) = \frac{5\tilde{C}e^2}{128\pi\mu\tilde{\omega}^2(E_g - \hbar\tilde{\omega})^{7/2}}. \quad (12)$$

It is easily confirmed that the resonant part of $\chi^{(3)}(\omega)$ obeys the third derivative law of Aspnes and Rowe [16]: $\chi^{(3)}(\omega) \approx e^2/(24\mu\hbar\omega^2)\partial^3[\omega^2\chi^{(1)}(\omega)]/\partial\omega^3$. In figures 3 and 4, the imaginary part of the electro-optic spectrum $\Delta\varepsilon(\omega) \equiv \tilde{\varepsilon}_\Gamma(\omega; F) - \tilde{\varepsilon}_\Gamma(\omega; 0)$ is illustrated using polymethineimine as an example. The various parameters are taken as $\mu = 0.1 m_0$, $E_g = 2$ and $\hbar\Gamma = 0.02$ eV. Since l_P is roughly given by the dimension of the polymethineimine unit cell we set l_P equal to 3 and 0 Å in the polar and non-polar cases respectively. The value of the prefactor \tilde{C} is adjusted to $\tilde{C} = 333$ eV^{5/2} in order to have $\tilde{\varepsilon}_\Gamma(0) \approx 8$, which is a typical value for conjugated polymers. The calculations in figures 3 and 4 correspond to a low-field ($E_f = 0.005$ eV $\sim F = 5.8$ kV cm⁻¹) and high-field ($E_f = 0.03$ eV $\sim F = \pm 85$ kV cm⁻¹) case respectively. In the low-field case, the asymptotic spectra $\chi^{(2)} F$ and $\chi^{(2)} F + \chi^{(3)} F^2$ given

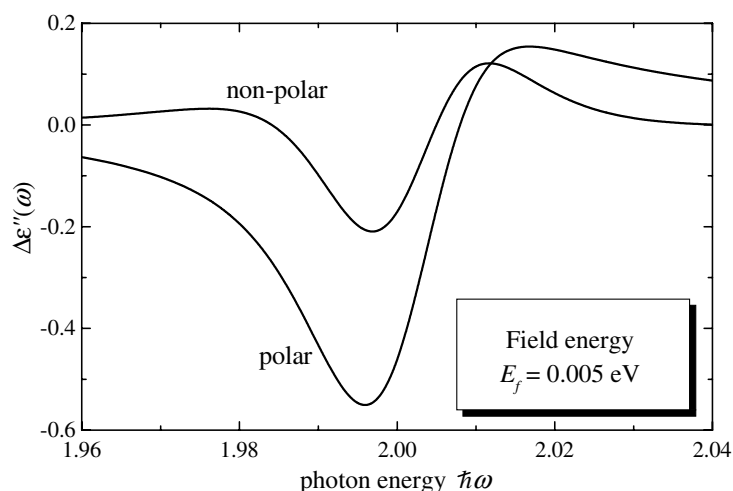


Figure 3. Imaginary part of the electro-optic spectrum $\Delta\varepsilon''(\omega)$ for polymethineimine in the vicinity of the band gap $E_g = 2$ eV. The spectra illustrate a low-field case, in which the field energy $E_f = 0.005$ eV (corresponding to $F = 5.8$ kV cm $^{-1}$) is less than the broadening $\hbar\Gamma = 0.02$ eV.

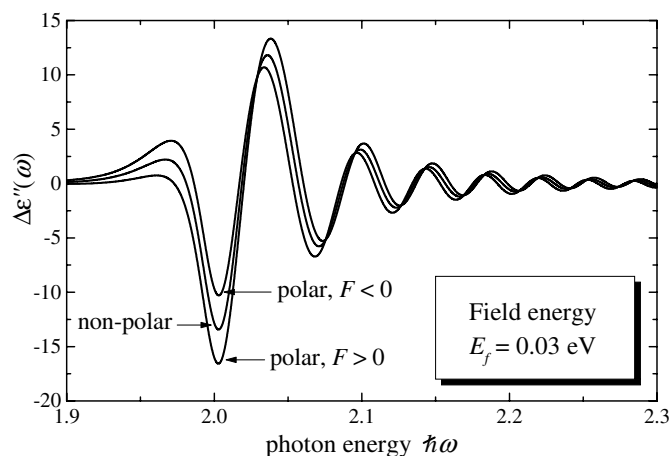


Figure 4. Same as figure 3, but for the high-field regime. The field energy $E_f = 0.03$ eV ($F = 85$ kV cm $^{-1}$) is larger than the broadening $\hbar\Gamma = 0.02$ eV. The characteristic Franz-Keldysh oscillations are clearly visible in non-polar as well as polar spectra. The sign dependence in the polar case is a result of linear and higher odd-order field terms.

by equations (11) and (12) are found to be practically indistinguishable from the exact results. Also, the effect of the applied field is seen to be larger in the polar case, as expected. The high-field case, on the other hand, is clearly in the non-perturbative regime. Pronounced oscillations are visible above the band gap in both the polar and non-polar spectra. A large effect of the sign of the field is noticed. In all three curves of figure 4, field-induced absorption is observed around $\hbar\omega = 1.97$ eV. The transition from the perturbative to the non-perturbative regime is expected to occur when the field energy E_f becomes comparable to the broadening $\hbar\Gamma = 0.02$ eV. Our findings are seen to be in agreement with this general rule. The relative significance of the polar corrections is seen to be smallest in the high-field case. This is reasonable since higher-order

terms start to dominate. In fact, it is found that for the oscillatory part, the main difference between polar and non-polar spectra is a shift of the former by approximately $\Delta(\hbar\omega) \approx el_p F$. The amplitude of the oscillations is not severely affected.

4. Conclusion

In conclusion, we have presented an analytic calculation of the optical properties of a one-dimensional polar semiconductor in the presence of an electrostatic field. The complex field-dependent dielectric constant including line broadening is expressed in terms of Airy functions. The polar corrections are proportional to a polarity length related to the conduction and valence band dipole moments. The characteristic signatures of the Franz–Keldysh effect in non-polar materials, i.e. induced absorption below the band gap and oscillatory modulation of the spectrum, are found in the polar case as well.

Acknowledgment

Financial support from the Danish Technical Science Council STVF, talent grant no 56-00-0290 is gratefully acknowledged.

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