Fermi resonance interface solitons

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The nonlinear dynamics of the interface between two layers of organic semiconductors is discussed for the case of the Fermi resonance, which occurs when the energy $\hbar\omega^c$ of excitation on one side of the interface is approximately equal to $2\hbar\omega^b$, where $\hbar\omega^b$ is the excitation energy on the other side. The Fermi resonance interaction across the interface gives rise to nonlinear plane waves, which propagate along the interface, and also to 2D solitons which are localized at the interface.

1. It is well known that the epitaxial growth of inorganic semiconductors is limited to materials with a small lattice mismatch. The organic materials, in contrast, are bound by weak van der Waals forces, which allows the layering of materials with different lattice constants. Great efforts have therefore been undertaken recently to create thin, strongly ordered, crystalline organic films and multilayer structures.[1–5] The theoretical analysis of linear and nonlinear optical properties of multilayer organic structures has also become topical and some problems in this field were discussed in recent papers.[6–14]

One of the mechanisms of a "hand-made" optical nonlinearity of multilayer organic structures, which was pointed out recently,[8,9] is based on the Fermi resonance between excitations of neighboring layers. In Refs. 9, 10, and 12 such interface Fermi resonance was discussed for the case in which the energy of two excitons $2\hbar\omega^b$ in one layer is close to the exciton energy, $\hbar\omega^c$, in the neighboring layer. In these papers the new states—quantum and classical Fermi resonance interface modes (FRIM)—were found. These modes appeared as a result of an intermolecular anharmonic interaction across the interface. This phenomenon extends the usual Fermi resonance in the bulk molecular crystals and can be important, as was shown in Refs. 8–14 in the investigations of the linear and nonlinear optical properties of multilayer structures.

In the limit of strong pumping, i.e., for large occupation numbers of excitations, it is natural to use a classical approximation suggested for the FRIM model in Refs. 8 and 10. It was shown in Ref. 10 that the anharmonic interaction under consideration can lead to bistability in the energy transmission through the interface. Using the very simple 1D model, it was demonstrated that there is a close connection between bistability and classical FRIM.

We can now extend this model to the 3D case with a 2D interface. We will consider the energy propagation along the interface.

2. We assume that the bilayered structure consists of two molecular crystals which are separated by a perfect plane interface. The c-type molecules occupy the sites of the simple cubic lattice to the right of the interface (n_x, n_y, n_z; $n_x=0, 1, 2,...$) and the b-type molecules occupy the sites of the lattice to the left of the interface (n_x, n_y, n_z; $n_x=-1, -2,...$). To demonstrate the appearance of the Fermi resonance interface solitons, we consider here a simple case of the Fermi resonance between c and b harmonic vibrations, assuming that $\hbar\omega^c \simeq 2\hbar\omega^b$. For this case the main anharmonic interaction between the c and b molecules corresponds to the cubic anharmonicity. It has the form

$$\hat{H}_{\text{int}}=\Gamma[c_{0},n_y,n_z(b^\dagger_{-1,n_y,n_z})^2+\text{H.c.}],$$

where $b^\dagger(b)$ and $c^\dagger(c)$ are the creation (annihilation) operators for the b and c excitations.

In the classical approximation we replace all operators by their mean values $\langle b_{n_xn_yn_z}\rangle = B_{n_xn_yn_z}$ and $\langle c_{n_xn_yn_z}\rangle = C_{n_xn_yn_z}$, where B and C are classical amplitudes of vibrations. In our model these variables satisfy the equations

$$i\partial B_{n_xn_yn_z}/\partial t-\omega^b B_{n_xn_yn_z}-V^b(B_{n_z-1,n_y,n_z}+B_{n_x}+1,n_y,n_z+B_{n_x,n_y-1.n_z}+B_{n_x,n_y+1,n_z}$$
$$+B_{n_x,n_{y,n_z-1}}+B_{n_x,n_y,n_z+1})=0 \qquad (1)$$

for the molecules in the bulk of the b crystal,

$$i\partial B_{-1,n_y,n_z}/\partial t-\omega^b B_{-1,n_y,n_z}-V^b(B_{-2,n_y,n_z}+B_{-1,n_y-1,n_z}+B_{-1,n_y+1,n_z}+B_{-1,n_y,n_z-1}$$
$$+B_{-1,n_y,n_z+1})-2\Gamma B^*_{-1,n_y,n_z}C_{0n_yn_z}=0 \qquad (2)$$

for the b molecules near the interface ($n_z=-1$),

$$i\partial C_{0,n_y,n_z}/\partial t-\omega^c C_{0,n_y,n_z}-V^c(C_{1,n_y,n_z}+C_{0,n_y-1,n_z}+C_{0,n_y+1,n_z}+C_{0,n_y,n_z-1}+C_{0,n_y,n_z+1})$$
$$-\Gamma B^2_{-1,n_y,n_z}=0 \qquad (3)$$

for the c molecules near the interface ($n_z=0$), and

$$i\partial C_{n_xn_yn_z}/\partial t-\omega^c C_{n_xn_yn_z}-V^c(C_{n_x-1,n_y,n_z}+C_{n_x+1,n_y,n_z}+C_{n_x,n_y-1n_z}+C_{n_x,n_y+1,n_z}$$
$$+C_{n_x,n_y,n_z-1}+C_{n_x,n_y,n_z+1})=0 \qquad (4)$$

for the molecules in the bulk of the c crystal.

We shall seek the solution, localized near the interface, in the form of a plane:

$$B_{n_xn_yn_z}=Be^{-\frac{i\omega}{2}t}e^{\kappa_b n_x}e^{\frac{i}{2}(k_yn_y+k_zn_z)},$$
$$C_{n_xn_yn_z}=Ce^{-i\omega t}e^{-\kappa_c n_x}e^{i(k_yn_y+k_zn_z)}. \qquad (5)$$

with $\kappa_b>0$ and $\kappa_c>0$. From Eqs. (1) and (4) we find

$$\omega^b-\omega/2+2V^b[\cosh\kappa_b+\cos(k_y/2)+\cos(k_x/2)]=0,$$
$$\omega^c-\omega+2V^c(\cosh\kappa_c+\cos k_y+\cos k_z)=0. \qquad (6)$$

These equations give us the values of κ_b and κ_c as functions of ω and (k_y, k_z). Equations (2) and (3) give the relationship between the variables B and C which can be written with the help of (6) in the form

$$2\Gamma B^*C = V^b B e^{\kappa_b}, \quad \Gamma B^2 = V^c C e^{\kappa_c}. \tag{7}$$

These relations yield immediately

$$I \equiv |B|^2 = \frac{V^b V^c}{2\Gamma^2} e^{\kappa_b+\kappa_c}. \tag{8}$$

As follows from (8), the quantities κ_b and κ_c are real in case of real V^b, V^c and Γ and they increase with increasing intensity I. The quantities $V^b e^{\kappa_b}$ and $V^c e^{\kappa_c}$ can be easily found from (6), which leads to the dispersion relation in an implicit form

$$8\Gamma^2 I = \left\{\frac{\omega}{2} - \omega^b - 2V^b[\cos(k_y/2)] + \cos(k_z/2)\right] + \left[\left(\frac{\omega}{2} - \omega^b - 2V^b(\cos(k_y/2) + \cos(k_z/2))\right)^2 - 4(V^b)^2\right]^{1/2}\}\{\omega - \omega^c - 2V^c(\cos k_y + \cos k_z) + [(\omega - \omega^c - 2V^c(\cos k_y + \cos k_z))^2 - 4(V^c)^2]^{1/2}\}. \tag{9}$$

If V^b and V^c vanish, we return to the two-molecule model discussed in Ref. 10. The signs in front of the roots correspond to the positive values of $\{\omega/2 - \omega^b - 2V^b[\cos(k_y/2) + \cos(k_z/2)]$ and $[\omega - \omega^c - 2V^c(\cos k_y + \cos k_z)]\}$; otherwise, they should be reversed. Such a choice leads to the correct limit as V^b, $V^c \to 0$.

3. In the long-wave limit $|k_y|, |k_z| \ll 1$, Eq. (9) leads to the quadratic dependence of ω on the wave numbers k_y and k_z. If we consider a nonlinear, nonuniform wave propagating along the interface in the z direction, then the variables B and C will depend on t and z and their equations of motion will have in the long-wave limit the form

$$\begin{aligned} &i\frac{\partial B}{\partial t} - \tilde{\omega}^b B - \tilde{V}^b \frac{\partial^2 B}{\partial z^2} - 2\Gamma B^* C = 0, \\ &i\frac{\partial C}{\partial t} - \tilde{\omega}^c C - \tilde{V}^c \frac{\partial^2 C}{\partial z^2} - \Gamma B^2 = 0, \end{aligned} \tag{10}$$

where $\tilde{\omega}^b$, $\tilde{\omega}^c$, V^b, and $\tilde{V}^c$ are constants determined by the dispersion relation in the limit of small $|k_z|$ and at $k_y \equiv 0$. These equations may be considered as equations describing the two-plane model with renormalized parameters.

We would like to demonstrate that the system under consideration has soliton excitations. To this end, we consider a very simple case in which the solution of Eqs. (10) has the form

$$B = F\exp[(-i\Omega t + ikz)/2], \quad C = \beta F\exp(-i\Omega t + ikz), \quad F = F(z - vt), \tag{11}$$

where β is a constant. Substitution of these expressions into (10) yields

$$(\Omega/2 - \tilde{\omega}^b + \tilde{V}^b k^2/4)F - i(v + \tilde{V}^b k)F' - \tilde{V}^b F'' - 2\Gamma F^2 \beta = 0, \tag{12}$$

$$(\Omega-\tilde{\omega}^c+\tilde{V}^c k^2)F-i(v+2\tilde{V}^c k)F'-\tilde{V}^c F''-\Gamma F^2/\beta=0.$$

There are two ways in which the imaginary parts of these equations can vanish:

$$\text{(i)}\quad k=0,\quad v=0,$$
$$\text{(ii)}\quad \tilde{V}^b=2\tilde{V}^c,\quad v=-\tilde{V}^b k=-2\tilde{V}^c k. \tag{13}$$

First, we consider the case (i). Equations (12) for F are compatible if

$$\frac{\Omega/2-\tilde{\omega}^b}{\Omega-\tilde{\omega}^c}=\frac{\tilde{V}^b}{\tilde{V}^c}=2\beta^2, \tag{14}$$

where β and Ω are given by

$$\beta=\pm\sqrt{\frac{\tilde{V}^b}{2\tilde{V}^c}},\quad \Omega=\frac{2(\tilde{\omega}^b\tilde{V}^c-\tilde{\omega}^c\tilde{V}^b)}{\tilde{V}^c-2\tilde{V}^b}. \tag{15}$$

In what follows we choose the positive sign for β. Then F will satisfy the equation

$$F''-\frac{2\tilde{\omega}^b-\omega^c}{\tilde{V}^c-2\tilde{V}^b}F+\Gamma\sqrt{\frac{2}{\tilde{V}^b\tilde{V}^c}}F^2=0. \tag{16}$$

Its integration gives (the integration constants are such that $F'\to 0$, $F\to 0$ as $z\to\infty$)

$$F=\frac{\alpha}{\cosh^2(\kappa z)}, \tag{17}$$

where

$$\alpha=\frac{3\sqrt{\tilde{V}^b\tilde{V}^c}}{2\sqrt{2}\Gamma}\times\frac{2\tilde{\omega}^b-\tilde{\omega}^c}{\tilde{V}^c-2\tilde{V}^b},\quad \kappa=\frac{1}{2}\left(\frac{2\tilde{\omega}^b-\tilde{\omega}^c}{\tilde{V}^c-2\tilde{V}^b}\right)^{1/2}. \tag{18}$$

Thus, we have found for real κ the soliton solution for the interface wave

$$B=\frac{\alpha e^{-i\Omega t/2}}{\cosh^2(\kappa z)},\quad C=\frac{\alpha\beta e^{-i\Omega t}}{\cosh^2(\kappa z)}, \tag{19}$$

where all the parameters are defined above. This solution corresponds to the soliton at rest. Apparently, it is a very special case of a more general soliton solution.

The case (ii) in (13) leads to a particular solution for a moving soliton. Now we have

$$\beta=\pm 1,\quad \Omega=\frac{2}{3}(2\tilde{\omega}^c-\tilde{\omega}^b)-\frac{\tilde{V}^b}{2}k^2. \tag{20}$$

Integration of the equation for F leads to the moving soliton solution:

$$B=\frac{\alpha\ \exp(-i\Omega t/2-ivz/2\tilde{V}^b)}{\cosh^2[\kappa(z-vt)]},\quad C=\frac{\alpha\exp(-i\Omega t-ivz/\tilde{V}^b)}{\cosh^2[\kappa(z-vt)]}, \tag{21}$$

where

$$\alpha=\frac{1}{2\Gamma}(\tilde{\omega}^c-2\tilde{\omega}^b),\quad \kappa=\left[\frac{\tilde{\omega}^c-2\tilde{\omega}^b}{6\tilde{V}^b}\right]^{1/2}. \tag{22}$$

As v goes to zero, we return to the solution (19) for the soliton at rest with $\tilde{V}^b=2\tilde{V}^c$. One may expect that there are soliton excitations for a more arbitrary choice of parameters which describe the system. This possibility will be discussed elsewhere.

In summary, we have found that there are Fermi resonance interface modes which propagate along the interface between two crystals, provided that their vibronic excitations satisfy the Fermi resonance condition. In the limit of strong excitations these modes can be described by classical theory, and for some parameters or frequencies they can exist as the localized soliton states. Such propagating modes can play an important role in the energy transmission along the interfaces.

[1]F. F. So, S. R. Forrest, Y. Q. Shi, and W. H. Steier, Appl. Phys. Lett. **56**, 674 (1990); F. F. So and S. R. Forrest, Phys. Rev. Lett. **66**, 2649 (1991).

[2]G. E. Collins, V. S. Williams, L.-K. Chau *et al.*, Synth. Metals **54**, 351 (1993).

[3]A. J. Dann, H. Hoshi, and Y. Maruyama, J. Appl. Phys. **67**, 1371 (1990).

[4]N. Karl and N. Sato, Mol. Cryst. Liquid Cryst. **218**, 79 (1992); M. Möbus and N. Karl, Thin Solid Films **215**, 213 (1992).

[5]H. Akimuchi, T. Inoshita, S. Hotta *et al.*, Appl. Phys. Lett. **62** (23), 3158 (1993).

[6]V. M. Agranovich, Mol. Cryst. Liq. Cryst. **230**, 13 (1993).

[7]V. M. Agranovich, R. D. Atanasov, and G. F. Bassani, Chem. Phys. Lett. **199**, 621 (1992).

[8]V. M. Agranovich, Phys. Scripta. **T49**, 699 (1993).

[9]V. M. Agranovich and O. A. Dubovsky, Chem. Phys. Lett. **210**, 458 (1993).

[10]V. M. Agranovich and J. B. Page, Phys. Lett. A **183**, N5/6 (1993).

[11]V. M. Agranovich, *Nonlinear Optics* (1994, in press).

[12]Th. Neidlinger, P. Reineker, V. M. Agranovich, and V. I. Yudson, *Nonlinear Optics* (1994, submitted).

[13]V. M. Agranovich, P. Reineker, and V. I. Yudson, *Synthetic Metals* (1994, in press).

[14]V. M. Agranovich and J. B. Page, BAPS (March, 1994).

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