Fermi resonance solitary wave on the interface between two layers of organic semiconductors

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The nonlinear dynamics on the interface between two layers of organic semiconductors is discussed for the case of Fermi resonance, which occurs when the excitation energy $h \omega_c$, on one side of the interface approximately equals $2h \omega_b$, where $h \omega_b$ is the excitation energy on the other side. In the long wave limit the nonlinear periodic waves can propagate in the form of solitons. A variational approach to the description of such solitary excitations is suggested, which can be applied in a broad range of system parameters.

I. INTRODUCTION

Due to fast progress in the technology of thin organic films and multilayer structures,1–3 the theoretical analysis of linear and nonlinear optical properties of such structures has become topical.4–6 For example, the case of Fermi resonance between excitations of neighboring layers, when the energy of two excitons $2h \omega_b$ in one layer is close to the exciton energy $h \omega_c$ in the neighboring layer, can be potentially interesting for nonlinear optics of such materials.5 In these papers it has been shown that these states—quantum and classical Fermi resonance interface modes—appear as a result of an intermolecular anharmonic interaction across the interface.

In the limit of strong pumping, i.e., for large occupation numbers of excitations that we consider here, it is natural to use a classical approximation. The corresponding classical equations of motion have a variety of nonlinear solutions describing propagation of excitations along the interface. In Ref. 6 the solitary wave solutions have been found for some particular choices of the parameters describing the system. One may ask if analogous excitations exist for arbitrary choices of the parameters that would be potentially important for applications. Here we shall investigate this problem with the use of a variational approach. We should note that the equations arising in this problem actually coincide with the equations of wave propagation in media with cascaded $\chi^{(2)}$ nonlinearities, which attracted much attention recently. We suppose that the variational approach suggested in the present paper proves Menyuk’s “robustness hypothesis” of solitons7 that a two-parameter family of solitonlike waves should exist in such systems. The variational approach leads immediately to the approximate two-parameter solutions of the equations under consideration.10

We assume that the bilayered structure consists of two molecular crystals that are separated by a perfect plane interface. The $b$ molecules occupy the sites of the simple cubic lattice below the interface and the $c$-type molecules occupy the sites of the lattice above the interface. We consider here the simplest case of Fermi resonance between $b$ and $c$ harmonic vibrations, assuming that $2h \omega_b \approx h \omega_c$. Optical vibrational modes are described by the classical complex amplitudes $B(x,t)$ and $C(x,t)$ corresponding to the vibrations of the two types of molecules separated by the interface. As shown in Ref. 10, the variables $B$ and $C$ satisfy the following equations:

$$\frac{\partial B}{\partial t} - i\tilde{\omega}_b B - V_b \frac{\partial^2 B}{\partial x^2} - 2\Gamma B^* C = 0,$$

$$\frac{\partial C}{\partial t} - i\tilde{\omega}_c C - V_c \frac{\partial^2 C}{\partial x^2} - \Gamma B^2 = 0,$$

(1)

where $x$ and $t$ are the coordinates along the interface and time, respectively, $V_b$ and $V_c$ are the transfer matrix elements of excitons within the bulk of $b$ and $c$ molecules, $\Gamma$ is the constant of interaction of the molecules through the interface, and $\tilde{\omega}_b = \omega_b + 4V_b$, $\tilde{\omega}_c = \omega_c + 4V_c$ are the renormalized frequencies. Equations (1) may be considered as equations describing the propagation of nonlinear waves in a two-plane model with renormalized parameters. As mentioned above, they can be transformed easily into equations for wave propagation in media with cascaded $\chi^{(2)}$ nonlinearities.7–11 This coincidence is rather natural since the second harmonic generation can be considered as a special case of Fermi resonance.

Equation (1) has the bright soliton solution6

$$B = \frac{\alpha \text{sgn}(\beta) e^{-i\Omega t/2}}{\cosh(\kappa x)}, \quad C = \frac{\alpha |\beta| e^{-i\Omega t}}{\cosh(\kappa x)},$$

(2)

where

$$\alpha = \frac{3\sqrt{V_b}V_c}{2\sqrt{2\Gamma}} \frac{2\tilde{\omega}_b - \tilde{\omega}_c}{V_c - 2V_b}, \quad \beta = \pm \sqrt{\frac{V_b}{2V_c}},$$

(3)

$$\Omega = \frac{2(\tilde{\omega}_b V_c - \tilde{\omega}_c V_b)}{V_c - 2V_b}, \quad \kappa^2 = \frac{1}{4} \frac{2\tilde{\omega}_b - \tilde{\omega}_c}{V_c - 2V_b} > 0.$$  

(4)

This solution corresponds to a soliton at rest. There exists also (see Ref. 6) another case, $V_b = 2V_c$, leading to particular solutions for moving solitons. In this case we have
\[
B = \frac{\alpha \exp(-i\Omega t/2 + ikx/2)}{\cosh^2[\kappa(x - vt)]},
\]
\[
C = \frac{\alpha \exp(-i\Omega t + ikx)}{\cosh^2[\kappa(x - vt)]},
\]
where
\[
\alpha = \frac{1}{2i}(\tilde{\omega}_c - 2\tilde{\omega}_b), \quad \beta = \pm 1, \quad v = -V_b k = -2V_c k
\]
and
\[
\Omega = \frac{2}{3}(2\tilde{\omega}_c - \tilde{\omega}_b) - \frac{V_b}{2k^2}, \quad \kappa^2 = \frac{\tilde{\omega}_c - 2\tilde{\omega}_b}{6V_b} > 0.
\]
As \(v\) approaches zero we return to the solutions (2)–(4) for the solitons at rest, however, with \(V_b = 2V_c\).

Formally, this solution is valid for any value of the frequency difference \(\tilde{\omega}_c - 2\tilde{\omega}_b\), but it may be unstable for sufficiently large mismatch \(\tilde{\omega}_c - 2\tilde{\omega}_b\). It is well known that in this case we have another possibility to obtain an asymptotically exact solution of Eq. (1). As many authors have shown,\(^9,11–13\) when the phase mismatch between waves \(B\) and \(C\) is large, the wave propagation is approximately described by the nonlinear Schrödinger (NLS) equation. Indeed, when \(\omega_c \gg \left(|V_c|, \omega_b, |\partial C/\partial t|, |C| \ll \Gamma B^2, \right)\) we obtain from the second equation in Eq. (1)
\[
C = -\frac{\Gamma}{\omega_c} B^2.
\]
Substituting this relation into the first of equation in (1) we have
\[
i\frac{\partial B}{\partial t} - \omega_b B - V_b \frac{\partial^2 B}{\partial x^2} + \frac{2\Gamma^2}{\omega_c} |B|^2 B = 0.
\]
This NLS equation has the well-known soliton solution
\[
B = \frac{\kappa}{\Gamma} \sqrt{-\omega_c V_b} \exp\left[-i(\Omega t - kx)/2\right],
\]
which depends on two parameters \(\kappa\) and \(k\), and where \(v\) and \(\Omega\) are given by
\[
v = -V_b k, \quad \Omega = 2\tilde{\omega}_b + 2V_b (k^2/2 - 4/\kappa^2).
\]
Note that the system (1) has the exact NLS solitonlike solution with \(v = k = 0\) if \(V_c = 0\):
\[
B = \frac{\kappa}{\Gamma} \sqrt{-\omega_c - \Omega} V_b \exp(-i\Omega t/2),
\]
\[
C = \frac{V_b \kappa^2}{\Gamma} \exp(-i\Omega t/2),
\]
where
\[
\Omega = 2\tilde{\omega}_b + 2V_b \kappa^2.
\]
It is correct for any value of \(\tilde{\omega}_c > \Omega, \ V_b < 0\), and depends only on one parameter \(\kappa\).

Thus, there exist several families of exact or asymptotically exact solutions of Eqs. (1). The solution (2) describes a soliton at rest and does not depend on any parameters. The solution (5) corresponds to a mobile soliton and depends on one parameter \(k\), but it exists only if \(V_b = 2V_c\). Finally, the solution of (10) and (11) depends on two parameters \(\kappa\) and \(k\) and it is only asymptotically exact for large values of \(\omega_c\). One may expect that in the system under consideration there are analogous solitonic excitations depending on two parameters and not constrained by any conditions. This possibility will be discussed in the next two sections by means of a variational approach. As we have seen, there are two families of solutions with different shapes of solitons — \(B\) is proportional to \(\text{sech}(\kappa x)\) and \(\text{sech}^2(\kappa x)\). Correspondingly, there are two families of variational solutions, which will be considered separately.

II. VARIATIONAL APPROACH TO FERMI RESONANCE INTERFACE SOLITONS: THE FIRST FAMILY OF SOLUTIONS

The variational approach is based\(^14\) on the possibility to represent Eq. (1) as Lagrange equations corresponding to the Lagrangian
\[
L = \int \left\{\frac{1}{2}(-iB^*B_t + iB^tB - iC^*C_t + iC^tC) + \tilde{\omega}_b B^*B + \tilde{\omega}_c C^*C - V_b B_x^2B_x - V_c C_x^2C_x + \Gamma(B^2B^* + B^2C^2)\right\} dx,
\]
where \(B_x = \partial B/\partial x, B_{xx} = \partial B/\partial x, \text{etc.}\)

Expressions (5) suggest the following form for the trial functions:
\[
B = \frac{b \exp(i\varphi/2)}{\cosh^2[\kappa(x - \xi)]}, \quad C = \frac{c \exp(i\varphi)}{\cosh^2[\kappa(x - \xi)]},
\]
where
\[
\varphi = k(x - \xi)/2 + \delta.
\]
Substitution of (13) into (12) yields
\[
L = \frac{4b^2}{3\kappa} \left[\tilde{\omega}_b - V_b \left(\frac{k^2}{4} + \frac{4}{5} \kappa^2\right) - \left(\frac{k}{2} \xi_t - \delta_t\right) + \frac{1}{8} \xi k_t\right] + \frac{4c^2}{3\kappa} \left[\tilde{\omega}_c - V_c \left(\frac{k^2}{4} + \frac{4}{5} \kappa^2\right) - \left(\frac{k}{2} \xi_t - \delta_t\right) + \frac{1}{8} \xi k_t\right] + \frac{2}{15} \frac{b^2 c}{\kappa}.
\]
The Lagrangian equations for the variables \(b, c, \delta, \xi, k, \kappa\) read
\[
\tilde{\omega}_b - V_b \left(\frac{k^2}{4} + \frac{4}{5} \kappa^2\right) - \left(\frac{k}{2} \xi_t - \delta_t\right) + \frac{1}{8} \xi k_t + \frac{4}{5} \Gamma c = 0,
\]
\[
\tilde{\omega}_c - V_c \left(\frac{k^2}{4} + \frac{4}{5} \kappa^2\right) - \left(\frac{k}{2} \xi_t - \delta_t\right) + \frac{1}{8} \xi k_t + \frac{4}{5} \Gamma b^2 c = 0.
\]
\[
\frac{d}{dt} \left( \frac{b^2 + 2c^2}{\kappa} \right) = 0, \tag{18}
\]
\[
\left( \frac{d}{dt} \frac{b^2 + 2c^2}{\kappa} \right) k + \frac{b^2 + 2c^2}{\kappa} \frac{dk}{dt} = 0, \tag{19}
\]
\[
\frac{d}{dt} \left( \frac{b^2 + 2c^2}{\kappa} - \delta_i \right) + \frac{b^2}{\kappa} (\xi_i + 2kV_b) + \frac{2c^2}{\kappa} (\xi_i + 4kV_c) = 0, \tag{20}
\]
\[
b^2 \left( \bar{\omega}_b - V_b \left( \frac{k^2}{4} + \frac{4}{5} \kappa^2 \right) \right) - \frac{1}{2} \left( k \xi_i - \delta_i \right) + \frac{1}{2} \xi k_i + \frac{8}{5} V_b b^2 \kappa^2 + \frac{8}{5} V_c c^2 + \frac{k}{2} \xi_i - \delta_i \right) + \frac{1}{2} \xi k_i + \frac{8}{5} \Gamma b^2 c = 0. \tag{21}
\]
From Eqs. (18) and (19) we get \(dk/dt = 0\), i.e., \(k = \text{const.}\). Then differentiation of the phase (14) with respect to time \(t\) yields the expression for the frequency \(\Omega\):
\[
\Omega = \frac{k}{2} \xi_i - \delta_i. \tag{22}
\]

From Eq. (20) we find the velocity
\[
v = \xi_i = -k \frac{V_b b^2 + 4V_c c^2}{b^2 + 2c^2}, \tag{23}
\]
and, hence,
\[
\Omega = -\delta_i - \frac{V_b b^2 + 4V_c c^2}{b^2 + 2c^2} k^2 / 2. \tag{24}
\]
Substitution of (16) and (17) into (21) yields the relation
\[
2(V_b b^2 + V_c c^2) \kappa^2 = \Gamma b^2 c, \tag{25}
\]
\[
\Omega(k, \kappa) = \omega_b + \frac{\omega_c}{2} + \frac{2}{5}(6V_b - V_c) \kappa^2 - \frac{1}{4}(V_b + 2V_c) k^2 \pm \sqrt{\left[ \omega_b - \omega_c \right] \left[ \omega_b + \omega_c \right] + \frac{2}{5}(6V_b - V_c) \kappa^2 - \frac{1}{4}(V_b - 2V_c) k^2}^2 + \frac{256}{25} V_b V_c \kappa^4. \tag{28}
\]

The sign before the square root depends on the sign of the expression in brackets and should be chosen such that (28) reproduces the exact solution (2) at \(k = 0\) and \(\kappa\) given by Eq. (4). A simple and useful formula representing the two first terms of the series expansion of Eq. (28) in powers of \(k^2\) for \(\kappa\) from Eq. (4) is given by
\[
\Omega = \frac{2(\bar{\omega}_b V_c - \bar{\omega}_c V_b)}{V_c - 2V_b} - \frac{3V_b V_c}{2(V_b + V_c)} k^2. \tag{29}
\]
\[
\text{It reproduces the exact solutions (4) and (7) in the two limiting cases } k = 0 \text{ and } V_b = 2V_c. \text{ If the parameters } V_b \text{ and } V_c \text{ are small compared to } |\omega_c - 2\omega_b|, \text{ Eq. (29) is a very good approximation for the exact dependence (28) of } \Omega(k) \text{ on } k. \text{ In Fig. 1 we have shown two plots for the function } \Omega(k), \text{ one corresponds to the exact solution (28) and the other one to its approximation (29). We see that the difference is very small for parameters typical for real materials.}^{1-3} \text{ [Of course, such excellent agreement is obtained only for values of } \kappa \text{ given by Eq. (4).]}
\]
Substitution of (29) and (4) into (25) and (26) yields the expressions for the amplitudes:
\[
b(k) \approx \frac{5}{4\Gamma} \sqrt{\frac{V_b V_c}{2} \left[ \frac{24}{5} k^2 - \frac{V_b - 2V_c}{V_b + V_c} \right]}, \tag{30}
\]
Again in the two cases of $k = 0$ and $V_b = 2V_c$ we return to the exact solutions of the preceding section.

### III. VARIATIONAL APPROACH TO FERMI RESONANCE INTERFACE SOLITONS: THE SECOND FAMILY OF SOLUTIONS

Now we shall start from the asymptotically exact solution, \( (8) \) and \( (10) \), of the NLS \( (9) \), which suggests the following form for the trial function:

\[
B = \frac{b \exp(i\varphi/2)}{\cosh[\kappa(x - \xi)]}, \quad C = \frac{c \exp(i\varphi)}{\cosh[\kappa(x - \xi)]},
\]

where \( \varphi \) is again given by \( (14) \), an analogous calculation as above gives

\[
\Omega(k, \kappa) = \frac{\omega_b}{2} + \left( V_b + \frac{2}{5}V_c \right) \kappa^2 - \frac{1}{4}(V_b + 2V_c)k^2 \mp \sqrt{\left[ \frac{\omega_b - \omega_c}{2} + \left( V_b - \frac{2}{5}V_c \right) \kappa^2 - \frac{1}{4}(V_b + 2V_c)k^2 \right]^2 + \frac{64}{15}V_bV_c\kappa^4}.
\]

The sign before the square root depends on the sign of the expression in brackets and must be chosen such that Eq. \( (25) \) reproduces Eq. \( (11) \) for \( |2\omega_b - \omega_c| \gg |V_b|, |V_c| \).

### IV. CONCLUSION

The results obtained in this paper give a rather precise and complete description of solitons propagating along the interface between two crystals, provided that their vibronic excitations satisfy the Fermi resonance condition. The variational approach leads to the two families of solitonic excitations depending on two parameters. Such propagating modes can play an important role in the energy transmission along the interface. Analogous solutions of the optical equations describe the cascaded \( \chi^{(2)} \) nonlinearity phenomena.\(^2\text{–}9,11\text{–}13\)

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10. In a recent paper (Ref. 11) the variational method has been applied to the investigation of a particular case of stationary solitons. Our approach takes into account the moving solitons as well. In addition, we use different trial functions, which permit us to reproduce the exact solutions in the corresponding limits of the interpolating variational solution.