Difference frequency Fermi resonance interface modes in organic multilayer structures

V.M. Agranovich\textsuperscript{a}, A.M. Kamchatnov\textsuperscript{a}, R.W. Munn\textsuperscript{b,}\textsuperscript{*}

\textsuperscript{a} Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow Region, 142190, Russia
\textsuperscript{b} Department of Chemistry, UMIST, Manchester M60 1QD, UK

Received 25 April 2002; in final form 27 June 2002

Abstract

Difference Fermi resonance interface modes occur in layered molecular materials when two excitations on one side of an interface differ in energy by an amount that matches approximately the energy of an excitation to which they are coupled on the other side, provided that the mismatch (detuning) is less in magnitude than the non-linear coupling across the interface. Under this resonance condition, the Schrödinger equation is formulated for a superposition of one-particle and two-particle states, and a set of coupled equations is derived for the allowed energies. The equations are solved for the general cases when there is only one layer on one side of the interface and an arbitrary number on the other side, and also for the case of two layers on either side. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 77.35; 73.20.-r

Keywords: Fermi resonance; Multilayer structures

1. Introduction

Departures from perfect symmetry in a lattice naturally lead to modifications of the states and energies of the lattice. Most of these modifications are essentially quantitative, but they can also be qualitative, leading to states characteristic of the imperfections rather than the underlying perfect lattice. In particular, point defects can lead to localized defect modes, while interfaces can lead to localized interface modes. Such modes can be important in characterizing the defect or interface, and they may also imply novel phenomena with potential practical applications.

Surface exciton states were explored many years ago in crystals of the aromatic hydrocarbons such as tetracene [1] and anthracene [2]. These states arise specifically because the dipole–dipole interactions between layers of molecules parallel to the natural cleavage plane fall off more rapidly with the separation between layers than do the corresponding site shifts that arise from the difference between the ground and excited state van der Waals interactions. The assignment of the states to surface excitations is confirmed by their sensitivity.
to surface layers of solidified permanent gases [3]. These experiments show how coupling across the interface between two molecular crystalline materials modifies the interface modes, even when there is no special relationship between the molecules on either side of the interface.

More recently, techniques have been developed for preparing multilayer structures of planar conjugated molecules [4]. These techniques can yield high-quality interfaces between an organic material and an inorganic crystal substrate or between two organic materials. Good interfaces are obtained more readily than between two inorganic crystals, because the relatively weak forces between the molecules make the requirements for epitaxy much less stringent. With these techniques, it is possible to fabricate interfaces between sets of molecules that have tailored energy differences or specific interactions. To assist in deciding when to undertake this significant experimental task, suitable theoretical analysis of different situations is desirable.

In particular, interesting phenomena may be expected when there is resonance between the energies of sets of excitations on either side of an interface between different materials, especially when there is non-linear coupling between the excitations. Previous work has explored the non-linear processes that occur when two molecular excitations on one side of the interface have a total energy in resonance with that of a single excitation on the other side of the interface. Coupling between these excitations across the interface can then give rise to Fermi resonance interface modes (FRIM) [5]. Provided the coupling is strong enough relative to the couplings between excitations on the same side of the interface that gives rise to the conventional energy band, these modes can propagate along the interface and can give rise to solitons [6], which are characteristic of systems governed by interactions that are both dispersive and non-linear. Various properties of these solitons have been studied [7] after the customary passage from lattice equations to those of an equivalent continuum.

Here we explore a variation of the Fermi resonance situation that arises when two excitations on one side of an interface have a difference in energy that matches the energy of a single excitation on the other side of the interface. Given suitably strong non-linear coupling across the interface, this situation gives rise to what we call difference Fermi resonance interface modes (DFRIM). These have energies that lie outside the bands for the uncoupled excitations, and amplitudes that decay exponentially away from the interface. In Section 2 we present the model Hamiltonian for the system. Then in Section 3, we derive solutions for the situations where there is only one layer on one side of the interface or the other, and where there are only two layers on each side. The rather complicated DFRIM situation does not readily yield general solutions, but the cases treated here should suffice to indicate the main qualitative features for most practical purposes, given that interactions beyond nearest-neighbor molecules are usually negligible. In Section 4, we discuss our results and their applicability.

2. Model Hamiltonian

The model follows that described previously [5]. We use a one-dimensional representation of the multi-layer assembly in which each site index refers to a two-dimensional layer of molecules. There are \( r \) layers labelled \( n \) on the left-hand side of the interface, and \( R \) layers labelled \( N \) on the right-hand side. On the LHS there are two kinds of excitation: the operators \( a_y \) and \( a \) create and annihilate an excitation of energy \( e_a \), and the operators \( b_y \) and \( b \) create and annihilate an excitation of energy \( e_b \). On the RHS, the operators \( c_y \) and \( c \) create and annihilate an excitation of energy \( e_c \), and it is supposed that \( e_a - e_b \approx e_c \). Since only one excitation of every kind occupies any site, the statistics of excitations does not matter in this problem, and the theory under consideration can be applied equally well to bosons as to paulions or fermions. The Hamiltonian can be written as the sum of three terms:

\[
H = H_L + H_R + H_{\text{int}}.
\]

We use the subscript 1 to refer to the layer adjacent to the interface for each type of excitation, so that \( n, m = 1, 2, \ldots, r \) and \( N, M = 1, 2, \ldots, R \). Then the Hamiltonian for the LHS is
\[ H_L = \sum_n \left( e_a a_n^\dagger a_n + e_b b_n^\dagger b_n \right) + \sum_{nm} \left( V_{nm}^a a_n^\dagger a_m + V_{nm}^b b_n^\dagger b_m \right) \]

and that for the RHS is

\[ H_R = \sum_n e_c c_n^\dagger c_n + \sum_{NM} V_{NM}^c c_n^\dagger c_M, \]

in which the quantities \( V_{nm}^a \), \( V_{nm}^b \) and \( V_{NM}^c \) are the couplings between excitations of a given type that give rise to its normal energy band structure, while the coupling across the interface between the two sides is

\[ H_{int} = \Gamma(a_1^\dagger b_1 c_1 + a_1 b_1^\dagger c_1^\dagger), \]

where we have taken into account only the resonance interaction responsible for the effects under consideration. The allowed energies \( E \) are determined by the Schrödinger equation

\[ H \Psi = E \Psi, \]

where the wavefunction \( \Psi \) can be represented as a superposition of one-particle states \( \phi_n \) and two-particle states \( \psi_{nN} \):

\[ \Psi = \sum_n \phi_n a_n^\dagger |0\rangle + \sum_{nN} \psi_{nN} b_n^\dagger c_N^\dagger |0\rangle, \]

where \( |0\rangle \) is the vacuum state. Here the two-particle states described by the functions \( \psi_{nN} \) couple an excitation of type \( b \) at site \( n \) on the LHS and one of type \( c \) at site \( N \) on the RHS. Substitution in the Schrödinger equation (5) yields the following set of coupled equations:

\[ E \phi_n = e_a \phi_n + \sum_m V_{nm}^a \phi_m + \Gamma \psi_{11} \delta_{n1}, \]

\[ E \psi_{nN} = (e_b + e_c) \psi_{nN} + \sum_m V_{nm}^b \psi_{mN} + \sum_M V_{NM}^c \psi_{nM} + \Gamma \phi_1 \delta_{n1} \delta_{N1}. \]

Thus the system of equations describing non-linear interactions among the excitations is reduced to coupled equations that are linear in the amplitudes for the one and two-particle states.

The task is now to solve these equations for the case where \( e_a = e_b \approx e_c \), so that the detuning \( \beta \) defined as \( e_a - e_b - e_c \) by analogy with [8] is small compared with the individual energies. We introduce the variable \( x = E - e_b - e_c \), whence \( x + \beta = E - e_a \), which can be seen to emerge naturally as multipliers of the functions on the left-hand side of each member of the equation. For the physical situations envisaged, at least one of the materials will be composed of a small number of layers, and so the solutions of interest are required for various numbers of layers \( r \) and \( R \). We shall also assume nearest-neighbor coupling, so that \( V_{nm} = V_a \) for \( n = m \pm 1 \) and zero otherwise, with \( V_b \) and \( V_c \) defined similarly. Then in general for the one-particle states \( \phi_n \) we have

\[ (x + \beta) \phi_n = V_a [\phi_{n+1}(1 - \delta_{nr}) + \phi_{n-1}], \quad (n \geq 2), \]

where for the outermost layer \( n = r \) the Kronecker delta ensures that coupling is possible only on one side, while for the special case \( n = 1 \) we have

\[ (x + \beta) \phi_1 = V_a \phi_2(1 - \delta_{1r}) + \Gamma \psi_{11}. \]

For the two-particle states \( \psi_{nN} \) we have four sets of equations, depending on whether neither, either or both of \( n = 1 \) and \( N = 1 \) is satisfied:

\[ x \psi_{nN} = V_a [\psi_{n+1,N}(1 - \delta_{nr}) + \psi_{n-1,N}]; \]

\[ + V_b \psi_{n,N+1}(1 - \delta_{NR}) + \psi_{n,N-1}], \quad (n \geq 2, N \geq 2), \]

\[ x \psi_{1N} = V_b \psi_{2N}(1 - \delta_{1r}); \]

\[ + V_c \psi_{1,N+1}(1 - \delta_{NR}) + \psi_{1,N-1}], \quad (n = 1, N \geq 2), \]

\[ x \psi_{n1} = V_b \psi_{n+1,1}(1 - \delta_{nr}) + \psi_{n-1,1}]; \]

\[ + V_c \psi_{n,2}(1 - \delta_{1R}); \quad (n \geq 2, N = 1), \]

\[ x \psi_{11} = V_b \psi_{21}(1 - \delta_{1r}) + V_c \psi_{12}(1 - \delta_{1R}) + \Gamma \phi_1], \quad (n = 1, N = 1). \]

Since each equation allows for either layer to be outermost on its own side, each equation here has four different variants, depending on whether neither, either or both of \( n = r \) and \( N = R \) is satisfied.

3. Solutions

General solutions in the form of algebraic equations for the allowed energies \( E \) can be ob-
3.1. Single layer on LHS (r = 1)

For \( r = 1 \), there are no terms in \( V_o \) or \( V_b \), and for the LHS there is only the single function \( \phi_1 \), leaving a set of \( R \) equations for the functions \( \psi_{1N} \),

\[
(x + \beta)\phi_1 = \Gamma \psi_{11},
\]

\[
x\psi_{1N} = V_c[\psi_{1,N+1}(1 - \delta_N) + \psi_{1,N-1}], \quad (2 \leq N \leq R),
\]

\[x\psi_{11} = V_c\psi_{12} + \Gamma \phi_1.
\]

The system of equations can then be solved by systematic elimination of the functions \( \psi_{1N} \) starting from \( N = R \). The first elimination yields

\[
\psi_{1R} = (V_c/x)\psi_{1,R-1} = g^{(1)}_c(x)\psi_{1,R-1};
\]

the second yields

\[
x\psi_{1,R-1} = V_c\psi_{1,R} + V_c\psi_{1,R-2} = (V_c^2/x)\psi_{1,R-1} + V_c\psi_{1,R-2},
\]

that is

\[
\psi_{1,R-1} = \frac{V_c}{x - V_c^2/x}\psi_{R-2} = g^{(2)}_c(x)\psi_{1,R-2};
\]

and subsequent eliminations follow the same pattern, so that we obtain

\[
\psi_{1,R-N} = g^{(N+1)}_c(x)\psi_{1,R-N-1},
\]

and this sequence ends with the relation

\[
\psi_{12} = g^{(R-1)}_c(x)\psi_{11},
\]

where the \( g^{(N)}_c(x) \) are defined recursively by

\[
g^{(N)}_c(x) = \frac{V_c}{x - V_c^2g^{(N-1)}_c(x)}, \quad g^{(1)}_c(x) = \frac{V_c}{x}.
\]

From Eqs. (11) and (16) we obtain an equation for \( x \),

\[
x = V_cg^{(R-1)}_c(x) + \Gamma^2/(x + \beta)
\]

or making use of (17),

\[
(x + \beta)V_c = \Gamma^2g^{(R)}_c(x).
\]

We introduce dimensionless variables

\[
y = x/V_c, \quad \alpha = (\Gamma/V_c)^2, \quad \gamma = \beta/V_c
\]

and then Eq. (18) can be written in the form

\[
y + \gamma = \alpha g^{(R)}_c(y),
\]

where the \( g^{(N)}_c(y) \) are defined by

\[
g^{(N)}_c(y) = \frac{1}{y - g^{(N-1)}_c(y)}, \quad g^{(1)}_c(y) = \frac{1}{y}.
\]

Hence, we find a sequence of \( g^{(N)}_c(y) \):

\[
g^{(1)}_c(y) = \frac{1}{y}, \quad g^{(2)}_c(y) = \frac{y}{y^2 - 1}, \quad \ldots,
\]

\[
g^{(N)}_c(y) = \frac{P_N(y)}{Q_N(y)}, \quad \ldots,
\]

where \( P_N(y) \) and \( Q_N(y) \) are some polynomials in \( y \). Eq. (22) can therefore be expressed as

\[
P_N(y) = \frac{1}{yQ_{N-1}(y)/Q_{N-1}(y)} = \frac{Q_{N-1}(y)}{yQ_{N-1}(y) - P_{N-1}(y)},
\]

which shows that these polynomials can be defined recursively by

\[
P_N(y) = Q_{N-1}(y), \quad Q_N(y) = yQ_{N-1}(y) - Q_{N-2}(y),
\]

provided

\[
Q_0(y) = 1, \quad Q_1(y) = y.
\]

These formulas show that \( Q_N(y) \) can be expressed in terms of Chebyshev polynomials [9]:

\[
Q_N(y) = U_N(y/2),
\]

and the function \( g^{(R)}_c(y) \) is a ratio of two Chebyshev polynomials:

\[
g^{(R)}_c(y) = \frac{U_{R-1}(y/2)}{U_R(y/2)}.
\]

Then Eq. (21) can be written in the form

\[
(y + \gamma)U_{R}(y/2) = \alpha U_{R-1}(y/2).
\]

If there is no Fermi resonance interaction at the interface (\( x = 0 \)), then energy levels are determined by the equation

\[
(y + \gamma)U_{R}(y/2) = 0.
\]
If $\theta$ is defined by

$$y/2 = \cos \theta,$$  \hfill (31)

then we have [9]

$$U_R(y/2) = \frac{\sin[(R + 1)\theta]}{\sin \theta}$$

$$= 2^R \prod_{s=1}^{R} \left( \cos \theta - \cos \frac{s\pi}{R + 1} \right).$$  \hfill (32)

This equation gives the well-known energy levels

$$\frac{y}{2} = \frac{x}{2V_c} = \cos \frac{s\pi}{R + 1}, \quad s = 1, 2, \ldots, R,$$  \hfill (33)

for a standing wave of $c$-excitations in a linear chain with nearest-neighbor interactions. One additional level with $y = -\gamma \rho$ corresponds to the two-particle state $a + b$ at the site $n = 1$. The states (33) form a quasi-continuous band in the limit $R \to \infty$, defined by

$$-2 < y < 2, \quad (\text{or} \quad -2V_c < x < 2V_c).$$  \hfill (34)

When the Fermi resonance interaction is switched on (i.e., $\rho \neq 0$), the $R + 1$ levels of the system are determined by Eq. (29). They may be visualized as intersection points of the graph of the function

$$\frac{y + \gamma}{g_c^{(R)}(y)} = \frac{(y + \gamma)U_R(y/2)}{U_{R-1}(y/2)}$$  \hfill (35)

with the horizontal line $y = \alpha$. Here we recall that $\gamma$ is the detuning $\beta$ scaled by $V_c$, where $\beta$ is assumed to be small compared with the energies of the individual excitations, while $y$ is the energy relative to $e_k + e_{k'}$, also scaled by $V_c$. It turns out that the strongly localized non-linear DFRIM excitations correspond to values of $y^2 > 4$, whence it follows that $\gamma$ has negligible effect on these levels. Hence we concentrate on evaluating the levels of the system for zero detuning, i.e. $\gamma = 0$; the graphs whose intersections determine the levels are then as shown in Fig. 1.

For $R$ odd and small enough $\rho$, all $R + 1$ intersection points are located inside the band (34) and may be considered as disturbed states (33) plus the state $y = 0$ on the LHS of the system. For even $R$ all but one state can be found in a similar way, but the state $y = 0$ remains as a solution of the Eq. (29). Thus, for odd $R$ the Fermi resonance interaction splits the degenerate states with $y = 0$ into two states with different energies, while the others shift systematically. This transformation of the spectrum should be detectable in optical experiments and could then serve as a means of studying the Fermi resonance interaction with thin organic films.

For sufficiently large values of $\alpha$ for a given $R$ (for example, the critical value is $\alpha = 2.4$ for $R = 5$), two intersection points are “pushed out” of the band. These are DFRIM states, because the corresponding amplitudes $\psi_{1,N}$ decay exponentially as we move away from the interface.

To clarify this point, we consider the limit $R \to \infty$. Assuming that the limit $P_R(y)/Q_R(y)$ exists, we find from Eq. (22)

$$g_c(y) = \frac{1}{y - g_c(y)}, \quad \text{where} \quad g_c(y) \equiv \lim_{R \to \infty} g_c^{(R)}(y)$$

and hence

$$g_c(y) = \frac{y}{2} - \sqrt{\frac{y^2}{4} - 1},$$  \hfill (37)

where the sign before the square root is chosen so that we get the correct asymptotic behavior $g_c \sim 1/y$ in the limit $y \to \infty$, in accordance with the recursion relations. For negative $y < -2$ the signs must be reversed. Thus, Eq. (21) gives in this limit

$$y^2 = \frac{\alpha^2}{\alpha - 1},$$  \hfill (38)
that is, these states exist for \( x > 1 \). Since
\[
y^2 - 4 = \frac{(x - 2)^2}{x - 1} \geq 0,
\]
the second Eq. (11) gives
\[
\psi_{1N} = \psi_{1,N-1} e^{-x},
\]
then the two-part solution in the form
\[
x = 2V_c \cosh \kappa,
\]
and the other Eq. (11) give
\[
x = V_e^{-x} + 1/2.x.
\]
Writing these equations in terms of the variables (20), i.e.,
\[
y = e^x + e^{-x}, \quad y = e^{-x} + x/y,
\]
immediately yields the relation (38). In this limit, it can be verified from Eq. (11) that the amplitude \( \phi_1 \) of the single-particle component of the wavefunction is related to the two-particle part \( \psi_{11} \) by the factor \( 1 - \Gamma / V_c \). It follows that for strong non-linear coupling the single-particle and two-particle parts are comparable in magnitude. Thus, we have established that the particular Fermi resonance interaction studied here gives rise to DFRIM for large enough values of the coupling constant \( x = (\Gamma / V_c)^2 \). The critical value of \( x \) depends on \( R \) and tends to \( x = 1 \) as \( R \to \infty \).

### 3.2. Single layer on RHS \((R = 1)\)

For \( R = 1 \), there are no terms in \( V_c \), but the system of equations is more complicated, consisting of a set of \( r \) equations for the functions \( \phi_n \), coupled to a set of \( r \) equations for the functions \( \psi_n \):
\[
(x + \beta) \phi_n = V_a (\phi_{n+1} - \delta_{nr} + \phi_{n-1}), \quad (n \geq 2),
\]
\[
(x + \beta) \phi_1 = V_a \phi_2 + \Gamma \psi_1,
\]
\[
x \psi_{11} = V_b \psi_{21} + \Gamma \phi_1,
\]
\[
x \psi_{n1} = V_b (\psi_{n+1,1} - \delta_{nr} + \psi_{n-1,1}), \quad (n \geq 2).
\]
However, each set can again be solved iteratively, starting from \( r \), until two equations are reached that relate \( \phi_1 \) and \( \psi_{11} \). The iteration for the \( \phi_n \) and \( \psi_{n1} \) proceeds as in the previous case but in terms of \( V_a \) or \( V_b \) rather than \( V_c \), to yield eventually
\[
\phi_2 = g_a^{(r-1)}(x + \beta) \phi_1, \quad \psi_{21} = g_b^{(r-1)}(x) \psi_{11},
\]
where \( g_a^{(n)}(x) \) and \( g_b^{(n)}(x) \) are defined recursively by
\[
g_a^{(1)}(x) = V_a/x,
\]
\[
g_a^{(n)}(x) = V_a/(x - V_a \delta_a^{(n-1)}(x)),
\]
\[
g_b^{(1)}(x) = V_b/x,
\]
\[
g_b^{(n)}(x) = V_b/(x - V_b \delta_b^{(n-1)}(x)).
\]
Substitution of Eq. (45) into the other Eq. (44) gives a linear system
\[
(x + \beta) \phi_1 = V_a \delta_a^{(r-1)}(x + \beta) \phi_1 + \Gamma \psi_{11},
\]
\[
x \psi_{11} = V_b \delta_b^{(r-1)}(x) \psi_{11} + \Gamma \phi_1,
\]
with respect to the amplitudes \( \phi_1 \) and \( \psi_{11} \), or with the use of (46),
\[
\frac{V_a}{g_a^{(r)}(x + \beta)} \phi_1 = \Gamma \psi_{11}, \quad \frac{V_b}{g_b^{(r)}(x)} \psi_{11} = \Gamma \phi_1.
\]
This system has a nontrivial solution if \( x \) satisfies the equation
\[
g_a^{(r)}(x + \beta) g_b^{(r)}(x) = V_a V_b / \rho^2.
\]
Let us introduce dimensionless variables
\[
y = x/V_a, \quad x = (\Gamma / V_a)^2, \quad \gamma = \beta / V_a,
\]
\[
\rho = V_b / V_a, \quad x / V_b = y / \rho,
\]
so that
\[
g_a^{(r)}(y) = \frac{1}{y - g_a^{(r-1)}(y)} y,
\]
\[
g_a^{(1)}(y) = \frac{1}{y}, \quad g_a^{(r)}(y) = g_a^{(r)}(y / \rho).
\]
As in the preceding subsection, we can rewrite Eq. (49) in terms of the Chebyshev polynomials
\[
U_r(y + \gamma)/2 U_r(y/2 \rho) = (\gamma / \rho) U_{r-1}(y + \gamma)/2 U_{r-1}(y/2 \rho).
\]
and $b$ excitations. For $z \neq 0$ the eigenvalues of the energy $y$ can be found as the points of intersection of plots of two functions, namely

$$\frac{1}{g_a^{(r)}(y + \gamma)}g_a^{(r)}(y/\rho) \quad \text{and} \quad \alpha/\rho.$$  \hfill (53)

As previously, the strongly localized non-linear DFRIM excitations correspond to values of $y^2 > 4$, whence it follows that for small detuning $\beta$, the scaled parameter $\gamma$ has negligible effect on these levels. Hence we concentrate on evaluating the levels of the system for zero detuning, i.e., $\gamma = 0$.

We consider a number of illustrative examples.

(a) Let $V_a = V_b$ ($\rho = 1$). The corresponding plots are depicted in Fig. 2 for $r = 5$ and $\alpha = 1, 2, 3$. We see that as $\alpha$ increases, the two side states are pushed out from the band $-2 \leq y \leq 2$ and become strongly localized DFRIM states.

(b) Let $V_a = 2V_b$ ($\rho = 1/2$). The corresponding plots are depicted in Fig. 3 for $r = 5$ and $\alpha = 1, 2, 3$. The situation with DFRIM states is similar to the preceding case though the spectrum becomes more complicated inside the band because of overlap of two bands of different widths.

(c) Let $V_a = V_b/2$ ($\rho = 2$). The corresponding plots are shown in Fig. 4 for $r = 5$ and $\alpha = 4, 8, 12$. The situation differs from (b) only by the scale of the $y$-axis. The coupling constant in the chosen dimensionless units must be greater than in the preceding cases to form DFRIM states.

In the limit $r \to \infty$ we have

$$g_a(y) = \lim_{r \to \infty} g_a^{(r)}(y) = \frac{y}{2} - \sqrt{\frac{y^2}{4} - 1}. \hfill (54)$$

Solutions of the equation

$$1/g_a(y)g_a(y/\rho) = \alpha/\rho \hfill (55)$$

exist only for $y$ outside the widest band and for large enough values of the coupling constant $\alpha$. An example for $y > 2$ with $\rho = 1$ and $\alpha = 1, 2, 3$ is shown in Fig. 5.

3.3. Two layers on each side ($r = 2$, $R = 2$)

Once $r$ and $R$ can both exceed 1, the system of Eq. (11) becomes much less tractable. However, it
The system (56) gives at once

\[ x + \beta \phi_2 = V_a \phi_1, \]

\[ (x + \beta)\phi_1 = V_a \phi_2 + \Gamma \psi_{11}, \]  

\[ \psi_{22} = V_b \psi_{12} + V_c \psi_{21}, \]

\[ \psi_{12} = V_b \psi_{22} + V_c \psi_{11}, \]

\[ \psi_{21} = V_b \psi_{11} + V_c \psi_{22}, \]

\[ \psi_{11} = V_b \psi_{21} + V_c \psi_{12} + \Gamma \phi_1. \]  

The system (56) gives at once

\[ \phi_2 = \frac{V_a}{x + \beta} \phi_1, \]  

\[ \phi_1 = \frac{\Gamma}{x + \beta - V_b^2/(x + \beta)} \psi_{11}, \]

\[ = \frac{\Gamma}{V_a} g_a^{(2)}(x + \beta) \psi_{11}. \]  

We have to eliminate \(\psi_{22}\) from the system (57) and express \(\psi_{12}\) and \(\psi_{21}\) in terms of \(\psi_{11}\):

\[ \psi_{22} = (V_b/x) \psi_{12} + (V_c/x) \psi_{21}, \]

\[ \psi_{12} = \frac{g_b^{(2)}(x)}{V_b V_c [1 - g_b^{(1)}(x) g_c^{(1)}(x) g_b^{(2)}(x) g_c^{(2)}(x)]} \psi_{11}, \]

\[ \psi_{21} = \frac{g_c^{(2)}(x)}{V_b V_c [1 - g_b^{(1)}(x) g_c^{(1)}(x) g_b^{(2)}(x) g_c^{(2)}(x)]} \psi_{11}. \]  

Then substitution of Eqs. (60) and (62) into Eq. (58) yields the equation for \(x\)

\[ x = (V_b g_b^{(2)}(x) (V_c^2 + V_b^2 g_b^{(1)}(x) g_c^{(2)}(x))) \]

\[ + V_b g_b^{(2)}(x) (V_c^2 + V_c^2 g_c^{(1)}(x) g_b^{(2)}(x))) \]

\[ / (V_b V_c [1 - g_b^{(1)}(x) g_c^{(1)}(x) g_b^{(2)}(x) g_c^{(2)}(x)]) \]

\[ + ((\Gamma^2 / V_a) g_a^{(2)}(x + \beta)). \]  

To investigate this equation graphically, we confine ourselves to the simplest case \(V_b = V_c = V_a = V\) and introduce the dimensionless variables

\[ y = x/V, \quad \alpha = \Gamma^2 / V^2. \]  

As previously we also neglect the scaled detuning \(\gamma = \beta / V\). Then using the expressions

\[ g^{(1)} = \frac{1}{y}, \quad g^{(2)} = \frac{y}{y^2 - 1}. \]  

Eq. (63) takes the form

\[ (y^2 - 1)(y^2 - 4) \]  

\[ \frac{y^2 - 2}{y^2 - 2} = \alpha. \]  

For \(\alpha = 0\) we obtain the one- and two-particle states \(y = \pm 1, \ y = \pm 2\), which are solutions of the systems (56)–(58) with \(\Gamma = 0\). For \(\alpha \neq 0\) the eigenenergies can be visualized as the points of intersection of the functions on the LHS and RHS of Eq. (65), respectively (see Fig. 6).

For this few-particle system it is difficult to speak about “bands” and DFRIM states. But the change of energies with increase of the coupling constant \(\alpha\) of Fermi resonance interaction is clearly seen.
4. Discussion

In this paper, we have identified the phenomenon of difference Fermi resonance interface modes in layered molecular materials. Under the condition that the detuning is smaller than the non-linear coupling across the interface, we have formulated the corresponding time-independent Schrödinger equation for a superposition of one-particle and two-particle states, and have derived a set of coupled equations for the allowed energies. We have solved the equations for the general cases when there is only one layer on one side of the interface and an arbitrary number on the other side, and also for the case of two layers on each side.

The key issue is how the allowed energies depend on the parameter $\Gamma$ that couples the excitations across the interface. For zero coupling, the energies are just those of the separate layered materials on each side of the interface. We have found that for large enough values of the coupling parameter relative to the coupling between molecules on the same side of the interface, the difference Fermi resonance interaction gives rise to modes localized at the interface. These features depend in the first instance on the basic difference Fermi resonance energy criterion $e_a - e_b \approx e_c$. We have formulated the problem in terms of the detuning $\beta$ defined as $e_a - e_b - e_c$, which measures the deviation from exact resonance. However, sufficiently small detuning has only a minor quantitative effect on the DFRIM. Although formally the basic equations could be solved for arbitrary values of the detuning, the initial Hamiltonian was written assuming that the difference Fermi resonance condition $\beta \leq \Gamma$ is satisfied. Therefore, the properties of the new DFRIM modes can conveniently be illustrated for the case of strictly zero detuning, as in the figures presented here. These modes require strong coupling between molecules on opposite sides of the interface, and a correspondingly high energy relative to the resonant energy $e_b + e_c$, whereas the detuning is assumed to be small relative to the resonant energy. In the opposite formal limit, sufficiently large values of $\beta$ cannot satisfy the basic physical condition for Fermi resonance with only three levels, and we have not treated it here.

The energy difference $e_a - e_b \approx e_c$ could relate electronic states when an excited-state energy $e_c$ on one side matches the difference between two excited-state energies $e_a$ and $e_b$ on the other side, i.e., when an excitation from the ground state on one side of the interface has an energy that matches that of an excitation from an excited state on the other. Spectroscopy and quantum chemistry of aromatic molecules are very well developed and could easily explore pairs of molecules that satisfy this criterion.

Difference Fermi resonance could also involve vibrational states, which are numerous in molecular systems because of the many molecular modes. For example, two stretching modes could differ in energy by that of a bending or twisting mode. Molecules suitable for deposition in multilayer structures typically have planar polycyclic conjugated structures that might yield a hundred vibrational modes with energies from 20 to 400 meV. The weak interactions between molecules also ensure that molecular phonon bands are narrow, so that the strength of the coupling across the interface could easily exceed the bandwidth. Lattice modes are also available to match the energy difference between two molecular modes. Alternatively, a vibronic state matches in energy the electronic state and vibrational mode from which it is constructed, and a similar matching can readily be anticipated between corresponding states of chemically similar molecules on either side of the interface. An electronic energy difference on one side of an interface could also match a vibrational excitation energy on the other side.

An intriguing example might be provided by the fullerene $C_{60}$. Rather intense electric dipole forbidden second-harmonic generation at a fundamental photon energy of 1.8 eV in $C_{60}$ is attributed to resonance enhanced molecular transitions of equal energy from the ground state to an intermediate excited state (magnetic dipole allowed) and from the intermediate state to a final excited state (electric dipole allowed) that then necessarily has an electric dipole allowed transition back to the ground state [10]. It would be interesting to try to match the energy difference between these two excitations to that in another molecular material. One could also envisage unusual phenomena arising when two fullerene multilayers are sepa-
rated by a suitable molecular monolayer across which difference Fermi resonance could occur.

In most cases, the coupling interaction across the interface would probably depend on dipolar coupling (electric, or occasionally magnetic as in the case of \( C_{60} \)). The calculation of planewise dipole sums appropriate to surfaces or layered materials has been treated in many publications, and techniques for molecular layers are well developed [11]. Calculations of this sort show that for electric dipole transitions of moderately high intensity the coupling energy between layers parallel to the natural cleavage plane in the aromatic hydrocarbon crystals is 0.25 to 0.5 eV. Compared with bandwidths of 1 meV for the lowest-energy internal modes [12], this coupling is certainly large enough to produce DFRIM. The calculations also show that planewise dipole sums fall off exponentially with the separation between planes and become negligible beyond neighboring layers. This indicates that as far as the DFRIM are concerned, with their strong localization at the interface, the present calculations, with one layer of either type of molecule on a semi-infinite crystal of the other, or just two layers of each type, should suffice to delineate at least semi-quantitatively the range of behavior to be expected for DFRIM.

By identifying the phenomenon of difference Fermi resonance interface modes, the present work provides a basis for exploring further phenomena associated with them. For example, the transformation of the spectrum (e.g., the splitting of degenerate states because of the interface interaction) may be used as an experimental tool for investigating the Fermi resonance interaction in crystalline organic thin films. Also, the difference Fermi resonance interaction transforms an incident \( c \) wave at the interface into \( a \) and \( b \) waves outgoing from the interface in opposite directions. For ordinary Fermi resonance interface modes it was found previously [6,7] that thin nonlinear films can also support localized soliton-like nonlinear waves analogous to the parametric cascading solitons in nonlinear optics [13] that have been observed experimentally [14]. Similar structures can therefore also be expected in three-wave Fermi resonance systems of the type considered in this paper.

Acknowledgements

V.M.A. and A.M.K. acknowledge partial support through Grant 97-1074 “Physics of Nanostructures” of the Russian Ministry of Science and Technology and the Program “Low-Dimensional Quantum Structures” of the Russian Academy of Sciences. This work was initiated during the tenure of a Royal Society Kapitza Fellowship by V.M.A. at UMIST.

References