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**ON THE DELICATE PROPERTIES OF EXCITONIC SURFACE STATES
IN MULTILAYER MOLECULAR CRYSTALS**

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ABSTRACT

The surface states of Frenkel excitons in semiinfinite systems of multilayer molecular crystals are investigated theoretically within the framework of the second nearest layer approximation (SNLA). It is shown that if the material parameters of crystals satisfy determined conditions they may exhibit two kinds of excitonic surface states in the system. This is the main reason for the delicate properties of energy levels as well as superradiant decay rates of surface excitons in the crystals. Our calculations are compared with experimental observations in anthracene crystals.

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For a long time theories of excitonic surface states in multilayer molecular crystals have been usually based on the nearest layer approximation (NLA) [1-4] exceptions are some brief discussions of the second nearest layer approximation (SNLA) [5,6]. The reasons for this are that the interlayer interaction falls off very rapidly with increasing separation between layers, and for a long time NLA has been sufficient to explain various experiments. Theoretically, in the framework of NLA, systems have no surface state if $|R| > |\Delta_1|$, where R is the matrix element for transfer of excitation between two nearest layers, and Δ_1 is the difference between energies of the bulk and surface excitons without taking into account the transfer energy between layers. If $|R| < |\Delta_1|$ there are two (two-fold degenerate) surface states in a symmetric finite system, and one surface state in a semiinfinite system. As a result, there is only one surface energy level for excitons in these systems. These surface states are localized at the first surface layer of the system. It is also well known, both theoretically and experimentally, that in reduced dimension systems the surface excitons can decay rapidly, so that their lifetimes are of about picosecond scales (see in Refs. [1,2,8-14] and references therein). The effects of rapid radiative decay of excitons are now commonly called the superradiance of excitons, and are related to the surface states of excitons. The main reason for the superradiant radiative decay of surface excitons is their instability with respect to the emission of surface states due to the absence of translational symmetry in the direction perpendicular to layers of systems. Calculations within NLA can also predict only one superradiant radiative decay rate of exciton in the above systems. For a long time, experimental observations have been in agreement with NLA calculations. However, with the rapid development of advanced manipulation technologies for semiconductors and organic materials we are able to observe delicate structures of elementary excitations near the band edge in the spectrum and their dynamics. For example, delicate structures in the reflection and luminescence spectra of anthracene crystals observed by Nozue et al [7] have shown that there are two different surface states of excitons, and their energy levels are $25310 \pm 1 \text{ cm}^{-1}$ and $25107.2 \pm \text{ cm}^{-1}$, and the bulk excitonic energy level is located at 25097 cm^{-1} . Correspondingly, the energy differences of the first and second surface excitons with respect to the bulk one are $\delta_1 = \omega_1 - E_0 = 213 \pm 1 \text{ cm}^{-1}$ and $\delta_2 = \omega_2 - E_0 = 10.2 \pm 0.2 \text{ cm}^{-1}$, respectively. Here : $\omega_1(\omega_2)$ and E_0 are the energies of the first(second) surface exciton and the bulk one, respectively. Another remarkable example of these delicate properties is the experimental observation of Aaviksoo et al [8] of the superradiance of 2D Frenkel excitons in multilayer organic quantum wells (MOQW's). In Ref. [8], by means of a time-resolution technique, picosecond time scale measurements at low temperature have shown superradiant decays of ≈ 2 psec for the first surface layer exciton and $\approx 15 \pm 2$ psec for the exciton from the second surface layer. Those delicate structures observed by Nozue et al [7] and Aaviksoo et al [8] cannot be understood in the framework of NLA where calculations can predict only

one surface energy level and one superradiant radiative decay rate of that surface exciton. Recently, there has been an NLA theory for excitonic surface states in nonsymmetric finite systems [15]. In such systems, as the two-fold degeneracy no longer exists, the system may have two different surface states, even in NLA. The theory in Ref. [15], however, cannot predict the delicate structures mentioned above. Very recently, we have developed a second nearest layer approximation theory for excitonic surface states in a symmetric system [16]. In Ref. [16] we make the first comprehensive classification of all classes of states within the NSLA and have successfully applied it to explain the above properties. In finite systems within the SNLA we need to solve five difference equations which are complicated and not very useful in applications. Moreover, in the experiments carried out by Nozue et al [7] and Aaviksoo et al [8] the number of layers in the samples are large for these systems to be considered as semiinfinite. In such situations we need to consider only three difference equations instead of five as in Ref. [16], and the application to realistic situations becomes simpler. We present here a SNLA theory for excitonic surface states for semiinfinite systems of molecular crystals and investigate the behavior of the first and second surface states. The main reason for the delicate structures mentioned above can be understood physically in the framework of SNLA. Our theory is valid for molecular crystals in general, however, we will concentrate on the case of anthracene crystal because the delicate properties were observed in that material [7,8].

Let us consider a semiinfinite system composed of parallel infinite molecular layers with the interlayer spacing d . It is assumed that an excitation in a molecule interacts with other molecules in the ground state and propagates via dipolar interactions only. The electric field of a layer of dipoles falls off very rapidly with perpendicular distance from layer. Accordingly, we take into account the first and second nearest layer interactions only.

The Hamiltonian of the systems can be written as [1-4,15,16] :

$$H = \sum_{\vec{k}} \sum_n \left[E_n(\vec{k}) B_{n\vec{k}}^\dagger B_{n\vec{k}} + \sum_{m \neq n} M_{mn}(\vec{k}) B_{m\vec{k}}^\dagger B_{n\vec{k}} \right] \quad (1)$$

where $B_{n\vec{k}}^\dagger (B_{n\vec{k}})$ is the creation (annihilation) operator of a two-dimensional exciton in the n th layer with energy $E_n(\vec{k})$ and two-dimensional wave vector \vec{k} and M_{mn} is the matrix element for the transfer of the excitation from the n th to the m th layer. In NLA, M_{mn} has two equivalent contributions $R\delta_{m,n+1}$ and $R\delta_{m,n-1}$ regarded as the nearest layer interactions. In SNLA, it has four contributions, i.e., two of the nearest layer interactions, and two others $S\delta_{m,n+2}$ and $S\delta_{m,n-2}$ which are regarded as the second nearest layer interactions. R and S are called the nearest and second nearest layer interaction parameters, respectively. As only the first and second nearest layer interactions are taken into account, it can be assumed that the system consists of only two surface layers, one first top-surface layer (called the first layer) with energy $E_1(\vec{k})$ and one second top-surface

layer (called the second layer) with energy $E_2(\vec{k})$. The other layers of the system are given the same energy $E_{n \geq 3} = E_0(\vec{k})$ and are called internal layers. Here, it should be noted that $E_n(\vec{k})$ is the energy of the exciton in the n th layer ignoring the transfer energy between layers.

When the interlayer interactions are taken into account, an excitation can propagate from layer to layer. As a result the excitation belongs to the whole system rather than to separate layers. In this case the eigenfunction of the whole system can be written as

$$\Psi_{\vec{k}} = \sum_{n=1}^{\infty} \varphi_n(\vec{k}) B_{n\vec{k}}^\dagger |0\rangle, \quad (2)$$

where the envelope functions $\varphi_n(\vec{k})$ are to be determined so that the Schrödinger equation

$$H\Psi_{\vec{k}} = \omega_{\vec{k}}\Psi_{\vec{k}} \quad (3)$$

is satisfied with $\omega_{\vec{k}}$ denoting the eigenenergy of the whole structure (with $h = 1$). Substituting Eq. (1) and (2) into Eq. (3) we get the following three difference equations for the eigenenergy ω and the envelope function of the eigenstate φ_n (the wave vector \vec{k} of the motion in layer planes is omitted for brevity from now on) :

$$(\omega - E_n)\varphi_n = R(\varphi_{n+1} + \varphi_{n-1}) + S(\varphi_{n+2} + \varphi_{n-2}), \quad \text{for } n > 2 \quad (4)$$

$$(\omega - E_1)\varphi_1 = R\varphi_2 + S\varphi_3, \quad (5)$$

$$(\omega - E_2)\varphi_2 = R(\varphi_1 + \varphi_3) + S\varphi_4. \quad (6)$$

Eq. (4) is the general difference equation in SNLA, and Eqs. (5) and (6) are boundary conditions of the system under consideration. Note that in a finite system there are four boundary conditions.

Using the standard method of solving difference equations [5,15,16] we first look for the general solution of Eq. (4) in the form of a linear combination of four functions x, x^*, x^{-1} and x^{*-1} , where the function x has the following form

$$x = \exp[i(p + i\gamma)nd], \quad (7)$$

and then require that it satisfies the boundary equations. In Eq. (7) p and γ are real quantities and their allowed values are to be determined by solving combinations of Eq. (4) with Eqs. (5,6). The substitution of the general solution into Eq. (4) and the use of (7) gives :

$$\omega - E_0 = 2R \cos[(p + i\gamma)] + 2S \cos[2(p + i\gamma)]. \quad (8)$$

Hereafter p and γ are used in the unit of the interlayer spacing d . Eq. (8) is a second order equation in $\cos(p + i\gamma)$. Hence, for the fixed value of ω we have two pairs of (p, γ) satisfying the equation as long as S is finite. This is the first difference between SNLA and

NLA. The dispersion relation $\omega(p, \gamma)$ of the exciton is determined by using the allowed values of (p, γ) in Eq. (8), in general, or in Eqs. (10-12) for each class of state as we do below. Because ω, E_0, R and S are real quantities, the imaginary part in the right-hand side of Eq. (8) must vanish, leading to the following condition for p and γ :

$$\sin(p) \sinh(\gamma)[R + 4S \cos(p) \cosh(\gamma)] = 0. \quad (9)$$

Substitution of the general solution into the difference equation (4) and the use of Eq. (9) leads to the following possibilities :

- **Case (i)** : $p \neq 0, \gamma = 0$, and the eigenenergy is given by

$$\omega = E_0 + 2R \cos(p) + 2S \cos(2p), \quad (10)$$

- **Case (ii)** : $\gamma \neq 0, p = \pi j$ (j integer), and the eigenenergy is given by

$$\omega = E_0 + (-1)^j 2R \cosh(\gamma) + 2S \cosh(2\gamma), \quad (11)$$

- **Case (iii)** : $R + 4S \cos(p) \cosh(\gamma) = 0$, and the eigenenergy is given by

$$\omega = E_0 + 2R \cos(p) \cosh(\gamma) + 2S \cos(2p) \cosh(2\gamma). \quad (12)$$

In our previous paper [16] we have proved that there are two classes of band states and three classes of surface states depending upon the ratio $|R/4S|$ and a classification of states is necessary. In [16] we only deal with a model, symmetric finite system. However, the classification presented in that paper is based on the eigenenergy equations (10-12), which apply to both semiinfinite as well as symmetric finite systems. Therefore, we use this classification here and concentrate on the three classes of surface states.

Energically, from Eqs. (10-12) we have five classes of states [16]: (p, p') - and (p, γ) -band states (BS), $(\gamma j, \gamma' j)$ - , $(\gamma j, \gamma' j')$ - and (p, γ) -surface states (SS), depending upon the ratio $|R/4S|$. Here, it should be noted that the energy region extended by the eigenenergy function ω in Eq. (10) is the band energy, and the corresponding states must be classified as the band states. For brevity, let us look at Figs. 1a and 1b, which are the energy schemes for systems with $|R/4S| < 1$ and $|R/4S| > 1$, respectively. It can be clearly seen from Fig. 1a that in the band energy region B1 there are two values p and p' corresponding to one value of eigenenergy ω . Consequently, the corresponding states in this region are classified as the (p, p') -BS. Similarly, states belonging to B2 are classified as (p, γ) -BS. In Ref. [6] Mahan and Obermair discussed only one class of states which are just the (p, p') -BS above. This class of states appears if the condition $|R/4S| < 1$ holds. Therefore, if we consider only the (p, p') -BS we do not have enough information about the band states of the systems. In Fig. 1b (with $|R/4S| > 1$) there is only one band energy region B2 of (p, γ) -BS. Regarding the surface states, we have three classes : S1 is the energy region of

class $(\gamma j, \gamma' j)$ -SS as in this region, corresponding to one value of ω (given by Eq. (11)), there are two values of γ and γ' with the same integer value of j satisfying the sign rule $(-1)^j \text{Sign}(R) \text{Sign}(S) = -1$ (sign rule 1). Similarly, we classify states corresponding to energy regions S2 and S3 are classes of $(\gamma j, \gamma' j')$ -SS and (p, γ) -SS, respectively. In the case of class $(\gamma j, \gamma' j')$ -SS, j and j' must satisfy the sign rule 2 as $(-1)^j (-1)^{j'} = -1$. In Figs. 1a and 1b, the quantities $\Omega_1 = 2(|R| - |S|)$, $\Omega_2 = 2(|R| + |S|)$ and $\Omega_m = (R^2 + 8S^2)/4|S|$.

Now let us investigate the surface states of the system. First, we determine the allowed states, i.e., the allowed values of (p, γ) (called allowed values) defined in Eq. (7) as well as the envelope functions of eigenstates φ_n . We then consider the behaviour of the surface states and evaluate the delicate structures related to the surface states. From the general solution of the difference equation, it is easy to establish the following forms of the envelope functions for three surface classes as follows :

$$\varphi_n(\gamma j, \gamma' j) = (-1)^{nj} \left[\alpha_1 e^{-n\gamma} + \alpha'_1 e^{-n\gamma'} \right], \quad (13)$$

$$\varphi_n(\gamma j, \gamma' j') = (-1)^{nj} \alpha_2 e^{-n\gamma} + (-1)^{nj'} \alpha'_2 e^{-n\gamma'}, \quad (14)$$

$$\varphi_n(p, \gamma) = \left[\alpha_3 \cos(pn) + \alpha'_3 \sin(pn) \right] e^{-n\gamma}, \quad (15)$$

where $\alpha_i (\alpha'_i)$ are coefficients of envelope functions which must be determined.

At this point we wish to stress that in their famous paper [5] Koster and Slater predicted that there are only two classes of surface states, one is characterized by two pure imaginary values, ((γ, γ') -SS), and the other is characterized by one complex value of wave vectors ((p, γ) - SS). However, as can be proved analytically from Eqs. (10-12) and clearly seen from Figs. 1a and 1b, there are three classes of surface states and in cases of two classes, $(\gamma j, \gamma' j)$ - and $(\gamma j, \gamma' j')$ -SS, besides two pure imaginary values of wave vectors (γ, γ') , we have to use integer values j (and j') to describe the surface states. In these cases, the integers j and j' play an important role in the forms of sign rules 1 and 2 above. Another argument of Koster and Slater is that they predicted the energy levels of states belonging to (γ, γ') - and (p, γ) -SS are always located in opposite sides of the band energy. This means that, if the energy levels of (γ, γ') -SS are above the top of band energy, then the energies of (p, γ) - SS are below the bottom of band energy, and vice versa (see Fig. 3 in Ref. [5]). As can be seen clearly from Figs. 1a and 1b, $(\gamma j, \gamma' j')$ - and (p, γ) -SS are always located on opposite sides of band energy, but $(\gamma j, \gamma' j)$ - and (p, γ) -SS are on the same side. In fact, the argument of the authors in Ref. [5] were formally based only on the eigenenergy equation Eq. (10). They did not have any concrete conditions like the Eq. (9) above.

Substituting the envelope functions into boundary equations, e.g., Eqs. (5,6), with the use of Eqs. (10- 12) we obtain equations which can determine the allowed values

of our systems (called state equations). Numerically solving these state equations of all classes, we obtain some conclusions about the number of surface states as well as their characteristics depending not only on the absolute values but also on the signs of parameters $R, S, \Delta_1 = E_0 - E_1$ and $\Delta_2 = E_0 - E_2$ as follows:

- (a). $|R| > |\Delta_1|$: no surface states
- (b). $|\Delta_1| > |R| > |\Delta_2|$: one surface state.
 - b1. $Sign(S) = Sign(\Delta_1)$: surface state belong to $(\gamma j, \gamma' j)$ - or (p, γ) -SS.
 - b2. $Sign(S) = -Sign(\Delta_1)$: surface state belong to $(\gamma j, \gamma' j')$ -SS.
- (c). $|\Delta_1| > |\Delta_2| > |R|$: two surface states.
 - c1. $Sign(S) = Sign(\Delta_1)$: surface states belong to $(\gamma j, \gamma' j)$ - and/or (p, γ) -SS.
 - c2. $Sign(S) = -Sign(\Delta_1)$: surface states belong to $(\gamma j, \gamma' j')$ -SS.

The surface energy levels are below (above) the bottom (top) of band energy if $S > 0 (< 0)$ in cases (b1) and (c1), and vice versa in cases (b2) and (c2). Note that the number of surface states of the systems may be changed depending upon the material parameters. The ratios of $|R|$ to $|\Delta_1|$ and $|\Delta_2|$ decide the number of surface states, while the signs of S and Δ_1 play an important role in determining the class of surface states, as well as the location of surface energy levels comparing with the band energy ones. In the cases (a) and (b) the physics is the same as in NLA. The new, and delicate properties come from case (c) in which the surface states are distinguished as the first and second ones. The first surface states have energies higher (lower) than those of second ones if surface states are above (below) the top (bottom) of the band energy. The first and second surface states may belong to the same class of states, but they may also belong to two different classes.

Once we have the allowed values of states, we can get the eigenenergy from Eqs. (10-12), and then use the boundary equations and the normalization requirement $|\Psi|^2 = \sum_n |\varphi_n|^2 = 1$ to determine the coefficients α_i, α'_i . The envelope functions of all classes are then determined. The behaviour of the first and second surface states is described in Fig. 2 with the parameters corresponding to anthracene crystal [8,16,17], i.e. $\Delta_1 = -204cm^{-1}$, $\Delta_2 = -6cm^{-1}$, $R = -5cm^{-1}$ and $S = -0.625cm^{-1}$. As can be clearly seen from Fig. 2, the first surface states (in this case belonging to (p, γ) - SS) are strongly localized in the first surface layer, and the amplitude of the envelope functions is very small at the second surface layer, and nearly equal to zero in the remaining part of systems. The envelope function of the second state (in this case - $(\gamma j, \gamma' j)$ -SS) behaves as a damped oscillation. Its amplitude is very small at the first layer, has a maximum at the second and is damped oscillating into layers far from the face of the system. The behaviour of the first and second surface states described above is very useful in understanding why the first and second surface excitons show the different radiative decay rates observed by Aaviksoo et al [8] as well as the differences between the surface and bulk energy levels as

in the experiment of Nozue et al [7]. One can see that the first excitonic surface states are strongly localized at the first surface layers, and nearly vanish over the other parts of the systems. Therefore, these states can radiatively decay emitting a radiation field outside the systems with a large oscillator strength due to coherent superposition of the transition dipole moments at each layer. Its strongly localize behaviour at the first layer is the main reason for the large energy difference between the first surface state and the band (propagation) one. The second states are less radiative than the first ones because the oscillating behaviour of the envelope function partially cancels out the transition dipole moment of each layer. This oscillation behaviour also makes the energy level of second states similar to that of band states or the propagation ones.

We are now in a position to evaluate quantitatively the delicate structures of energy levels as well as of the superradiance of surface excitons in an anthracene crystal. We choose the material parameters corresponding to the crystal as mentioned above $\Delta_1 = -204cm^{-1}$, $\Delta_2 = -6cm^{-1}$, $R = -5cm^{-1}$, and $S = -0.625cm^{-1}$. The discussion above about the behaviour of first and second surface states is applicable to the system. There are two surface energy levels in both systems. Once we have set of the material constants Δ_1 , Δ_2 , R , S we then solve the state equations to get these allowed values, and the eigenenergies. The envelope functions φ_{in} of allowed surface states can also be obtained ($i = 1, 2$ indicates the first and second state). The radiative decay rates of i - state exciton can be expressed in term of the electric dipole moment of the total system $\vec{P}_i = \sum_n \vec{\mu} \varphi_{in}$ and the envelope functions obtained analytically above. The transition dipole moment $\vec{\mu}$ per unit layer depends on the wave vector and the coherent range of the excitation in the plane. Here, however, we assume the constant $\vec{\mu}$ both for the first and second surface excitons and for each layer because the radiative decay of exciton with the in-plane wavevector nearly equal to zero is dominant. Then the relative magnitude of the radiative decay rates involves only the envelope functions of the first and second surface excitons φ_{1n} and φ_{2n} [16,18] :

$$\frac{\Gamma_1}{\Gamma_2} \approx \frac{|\vec{P}_1|^2}{|\vec{P}_2|^2} = \frac{\Gamma_0(L^*/u)^2 |\sum_n \varphi_{1,n}|^2}{\Gamma_0(L^*/u)^2 |\sum_n \varphi_{2,n}|^2} = \frac{|\sum_n \varphi_{1,n}|^2}{|\sum_n \varphi_{2,n}|^2} \quad (16)$$

Here, $\Gamma_1(\Gamma_2)$ is the radiative decay rate of the first (second) surface exciton. L^* is the coherent length of the two-dimensional exciton, Γ_0 is the radiative decay rate of a single molecule and u is the size of a unit cell. Numerical calculations with material parameters of anthracene we obtain $p = 1.79335$ and $\gamma = 2.8941$ for the first state ((p, γ) -SS) giving $\delta_1 = 204.14cm^{-1}$, and $\gamma = 0.53517$ and $\gamma' = 1.7094$ giving $\delta_2 = 9.45cm^{-1}$ for the second one ($(\gamma j, \gamma' j)$ -SS) and $\Gamma_1/\Gamma_2 = 7.6$. As already mentioned above the values $\delta_1 = 213 \pm 1cm^{-1}$ and $\delta_2 = 10.2 \pm 0.2cm^{-1}$ were observed by Nozue et al [7], and the difference in radiative decay rates $\Gamma_1/\Gamma_2 \sim 8$ was observed by Aaviksoo et al [8]. Using the anthracene parameters as $L^* = 700\text{\AA}$, $\Gamma_0 = 2 \times 10^8 sec^{-1}$ and $u = 7\text{\AA}$, the values

of radiative lifetimes for the first ($T_1 = 1/\Gamma_1$) and second surface excitons ($T_2 = 1/\Gamma_2$) can be estimated to be of an order of 1 picosecond and 10 picosecond, respectively. We neglect the nonradiative channels which is justified because the observed dephasing rate is of the same order of magnitude as the estimated radiative decay rate for the first surface exciton.

At this point there arises a question about the role of S as we already know the importance of R in conditions under which surface states may appear in systems. Let us consider $S = 0$ in the case (γ_j, γ'_j) -SS. The following argument is valid for all classes. Substituting the envelope function (13) into Eq. (6), we obtain an equation of the form $\Delta_2 \varphi_2 = 0$ if $S = 0$. In this case if $\Delta_2 \neq 0$ then $\varphi_2 = 0$ then from Eq. (5) (with $S = 0$) $\Rightarrow \varphi_1 = 0$ then from Eq.(6) (with $S = 0$) $\Rightarrow \varphi_3 = 0$, and then from Eq. (4) (with $S = 0$) we have $\varphi_n = 0$ for all n . Therefore, Δ_2 must be equal to zero if $S = 0$. In other words if $\Delta_2 \neq 0$ then $S \neq 0$. Because of that, if we need to understand the delicate structures due to the difference between the first and second surface layers, we should take into account the second nearest layer interaction, i.e., the SNLA.

In conclusion we have investigated theoretically the delicate properties of excitonic surface states within the SNLA theory in semiinfinite multilayer molecular crystals. We have found that there exist two kinds of excitonic surface states in crystals which have material parameters satisfying $|\Delta_1| > |\Delta_2| > |R|$. This is the reason for the delicate properties of energy levels as well as the superradiant decay rates of surface excitons. The experimental observations of energy levels and the superradiance of surface excitons in anthracene can be understood by the same equal footing. Furthermore, the semiinfinite model presented in this communication seems to be useful in applications.

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Figure Captions

Fig.1 Energy scheme of states with $|R/4S| < 1$. (a) : $R = -1.2cm^{-1}$ and $S = -0.6cm^{-1}$. (b) : $R = -5cm^{-1}$ and $S = -0.625cm^{-1}$. Case (i) : energy ω as function of p , solid curve; Case (ii): ω as function of γ , dash-dotted curves. Curves (+) and (-) correspond to $(-1)^j Sign(R)Sign(S) = +1$ and -1 , respectively. Case (iii) : ω as function of p , dashed curve.

Fig.2 Behaviour of the envelope function of the first (solid curve) and second (dashed curve) surface states in system II with the same parameters as $\Delta_1 = -204cm^{-1}$, $\Delta_2 = -6cm^{-1}$, $R = -5cm^{-1}$ and $S = -0.625cm^{-1}$.

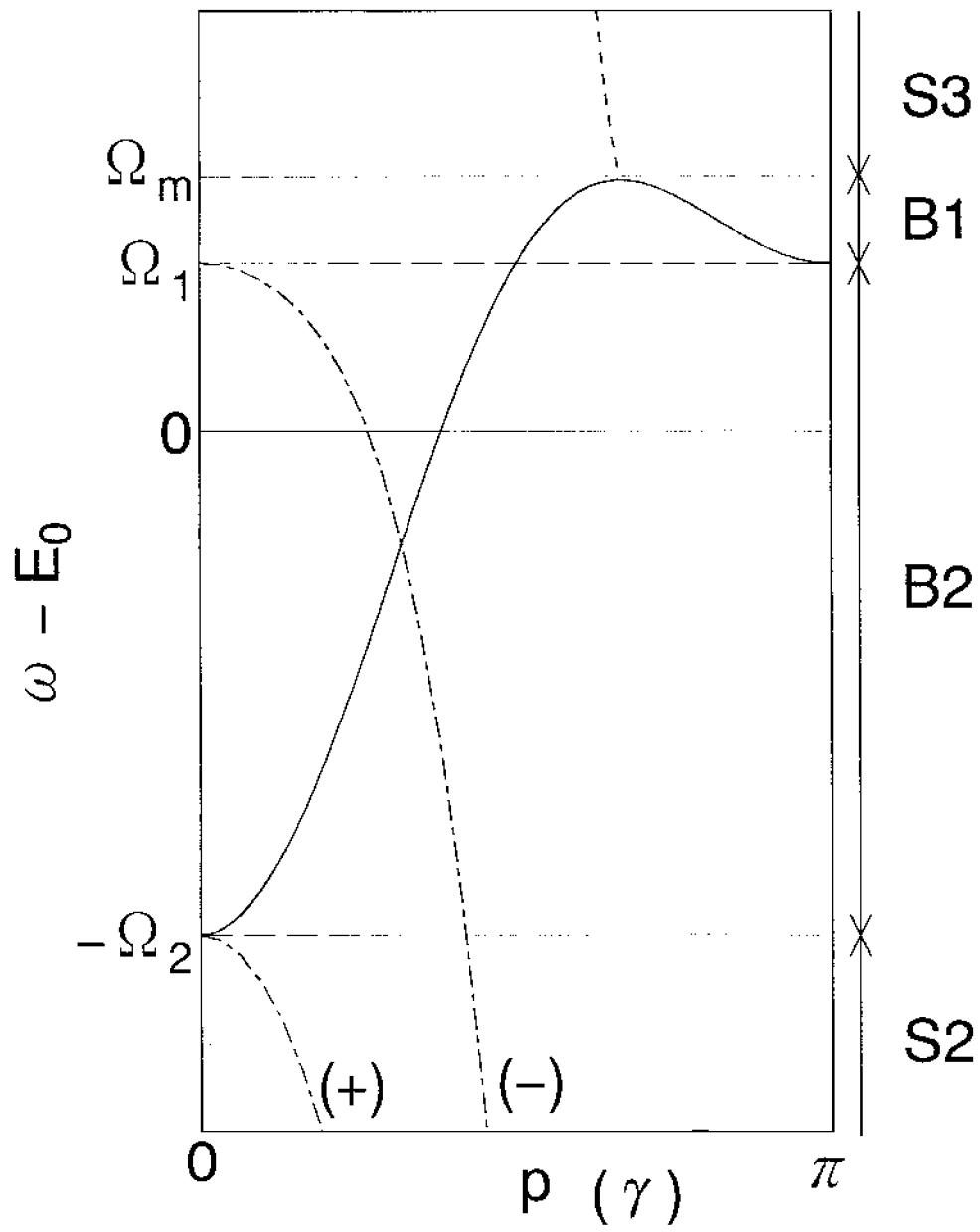


Fig.1a

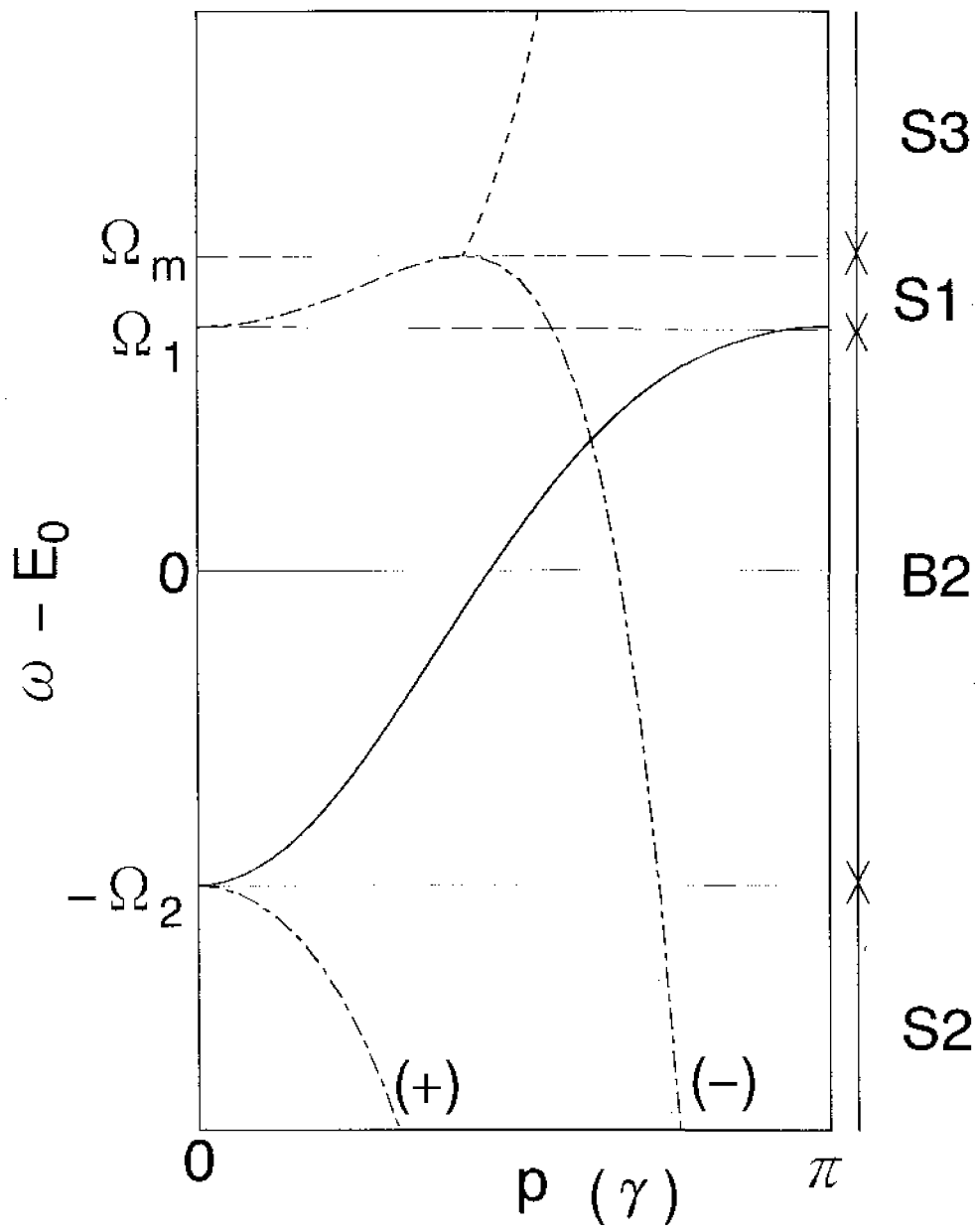


Fig.1b

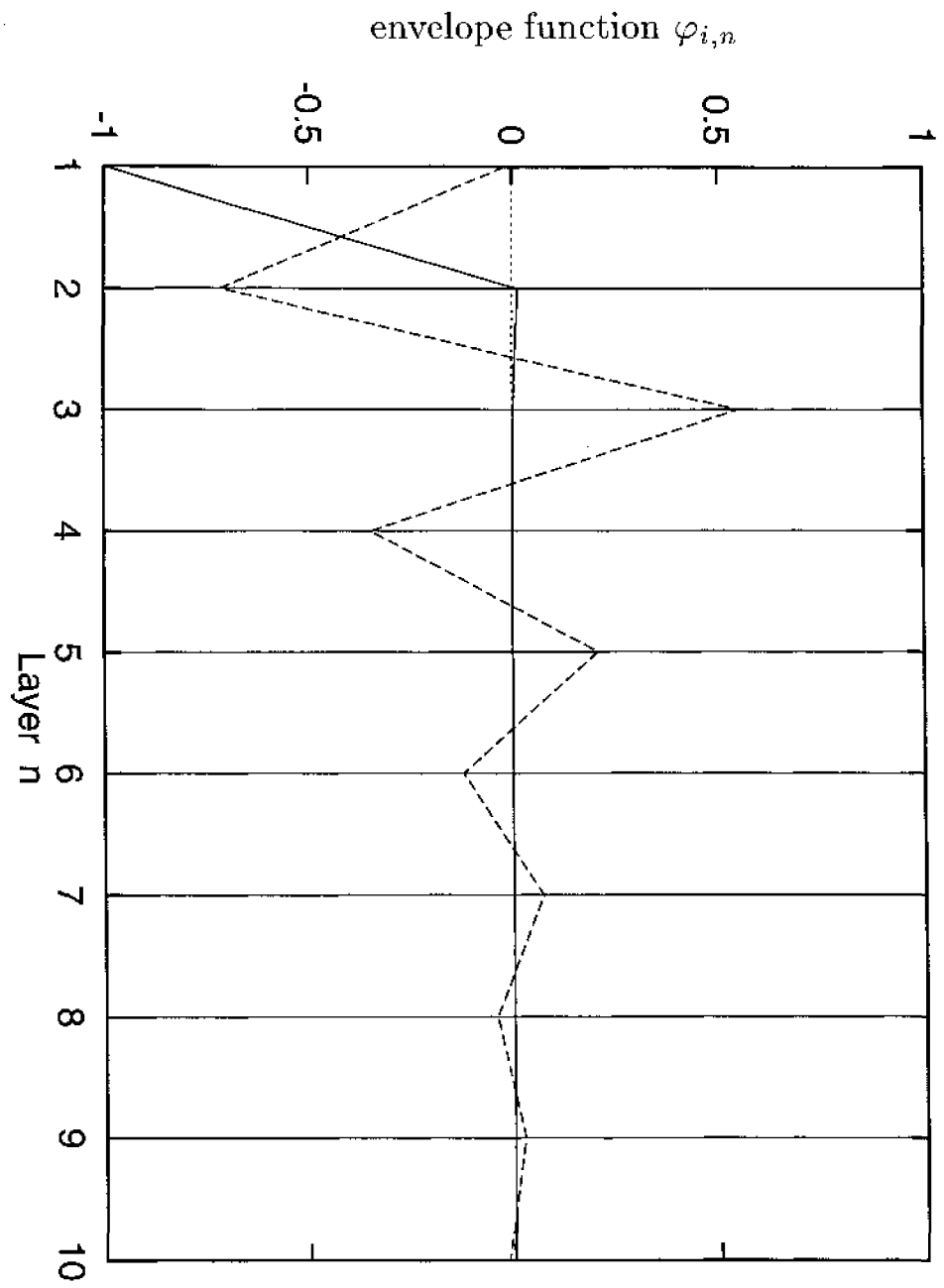


Fig.2