PHYSICAL REVIEW B VOLUME 54, NUMBER 4 15 JULY 1996-II

Theoretical investigation of excitonic surface states in multilayer organic quantum wells: Radiative decay rates of the first and second surface excitons

Nguyen Trung Dan and Eiichi Hanamura
Department of Applied Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

(Received 5 February 1996)

A theory of excitonic surface states in multilayer organic quantum wells is developed beyond the nearest-neighbor approximation. Eigenenergies and envelope functions of eigenstates of several kinds of surface states as well as band states are obtained, and the characteristics of surface states are clarified. The difference in super-radiant decay rates of the first and second surface excitons can be explained in the framework of the present theory. The results of numerical calculations are compared to the experimental data for two-dimensional Frenkel excitons in anthracene crystals. [S0163-1829(96)06128-0]

I. INTRODUCTION

The study of various types of mesoscopic structures, from semiconductor quantum dots to molecular multiple quantum wells, is a field of intense current interest. Semiconductor low-dimensional structures exhibit many interesting optical and transport properties that are of importance for applications in the optoelectric devices as well as for investigation of interactions and dynamics of confined carrier systems. Among those interesting properties, the effect of rapid radiative decay of excitons (picosecond and subpicosecond time scales of lifetimes) commonly now called super-radiance, has attracted much attention, both theoretically[1–3] and experimentally.[4–7] It is well known that in bulk crystals the exciton can interact with a photon which has the same wave vector due to the translation symmetry of the system. As a result, a polariton, i.e., a mixed state of the exciton and photon, is formed. The decay of excitons in the bulk crystal is possible only by a leak of the polariton through the surface of a crystal, or by radiative and nonradiative recombination at crystal imperfections. The situation in crystals of reduced dimensionality changes drastically. Theoretical investigations by Agranovich and Dubovski,[1] Hanamura,[2] and Andreani, Tassone, and Bassani[3] predicted the super-radiant decay of excitons in the low-dimensional structures. In Ref. 2 Wannier-Mott excitons have been pointed out to decay super-radiantly through its mesoscopic transition dipole moment in an order of a picosecond in GaAs quantum wells and a subpicosecond in CdS quantum wells. Experimental observations by Segawa *et al.*,[4] and Deveau *et al.*[5] were in agreement with the theory. Recently, great efforts have been made with the aim of creating strongly ordered crystalline organic thin-film and multilayer structures, which are very promising systems for various device applications as well as for studying molecular Frenkel and charge-transfer excitons.[8–11] Superradiance of two-dimensional (2D) Frenkel excitons in multilayer organic quantum wells (MOQW's) was first observed experimentally by Aaviksoo, Lippmaa, and Reinot[6] in the investigation of luminescence of a 2D Frenkel exciton localized in the outermost layers of anthracene crystals. In Ref. 6, by means of a time-resolution technique, picosecond time-scale measurements at low temperatures have shown super-radiant decays of about 2 psec or shorter for the first surface layer exciton, and of an order of 15 ± 2 psec for the exciton from the second surface layer. It is well known (for a review, see Ref. 12) that the exciton energy level of the first surface layer in anthracene is observed at 204 cm^{-1} above the bulk exciton, and that of second surface layer is also weakly observed at only 6 cm^{-1} above the bulk exciton one. The nature of these shifts is well understood as being due to the absence of neighbors for molecules in the surface layers and the change in the value of the site shift. There are availabe theories[13,14] which would explain how different the radiative decays of the exciton at the first surface layer are from the bulk one in MOQW's. The main reason for the super-radiant radiative decay of surface excitons is the instability property with respect to the emission of the excitonic surface states due to the absence of translational symmetry in the direction perpendicular to layer planes of MOQW's. However, there is still no answer to the question of why the radiative decay rate of the first surface exciton is different from that of the second surface layers, and also how much, as is explored in the observations of Aaviksoo, Lippmaa, and Reinot.[6] To our knowledge, for theories of excitonic surface states, the nearest-layer approximation (NLA) (Refs. 13–18) was usually used, except for some brief discussions on the second-nearest-layer approximation (SNLA) by Koster and Slater[17] and Mahan and Obermair.[18] In the framework of the NLA, the system has no surface state if $|R|>|\Delta_1|$, where R is the matrix element for the transfer of excitation between two nearest layers, and Δ_1 is the difference between energies of the bulk exciton and the first surface one without taking into account the transfer energy between layers. If $|R|<|\Delta_1|$ there are at most two surface states, which are localized near the two faces of finite thickness systems.[13–16] So far, theories of excitonic surface states have usually been based on assumptions of the nearest layer approximation. This is because the interlayer interaction, in fact, falls off very rapidly against separation between layers, and also that theories in the NLA are sufficient to explain various experiments. Another important reason for that is the complication as well as the difficulty in the SNLA and higher-order approximations. Such a situation was reported in the famous paper by Koster and Slater.[17] However,

© 1996 The American Physical Society

with the rapid development of advanced manipulation technologies of semiconductors and organic materials, and laser technologies, we are able to observe the delicate structures of elementary excitations near the band edge in the spectrum and their dynamics. For example, dynamics of several surface states in anthracene crystals were clarified by Aaviksoo, Lippmaa, and Reinot.[6] Another example of the delicate properties is the reflection and luminescence spectra of the anthracene crystal observed by Nozue, Kawaharada, and Goto.[19] These spectra show that the energy levels of the first surface and second surface excitons are 25310±1 and 25107.2±0.2 cm^{-1}, respectively, and the bulk exciton is located at 25097 cm^{-1}. Correspondingly, the energy differences of the first and second surface excitons with respect to the bulk one are $\delta_1=213\pm1$ cm^{-1} and $\delta_2=10.2\pm0.2$ cm^{-1}, respectively. However, for thick enough layers of organic crystals, we have only one optically active surface state, even if possible, in the framework of the NLA.[20] When the higher-order layer interactions are taken into account, electronic structures near the band edge are modified, and the higher-order surface states may possibly appear near the band edges even though the higher-order interactions are small.

In the present paper we investigate the behavior of the first and second surface excitons, and then attempt to understand the difference in the radiative decay rates of the surface excitons. This becomes possible only by taking into account the propagation effects of elementary excitation not only between nearest layers but also second-nearest layers. To do this, we develop a theory of excitonic surface states in the framework of the SNLA. It is easy to extend the SNLA to general cases. The results of the present paper show that in the SNLA, there are five classes of states: two of band states and three of surface states, instead of two of surface states as in the paper of Koster and Slater. Furthermore, the results also show that the case which was discussed by Mahan and Obermair is only one special case of our theory. The total number of states of the system is not changed, but the number of surface states can be changed importantly depending upon material constants. Now we have conditions for the existence of at most four surface states in a finite thickness system. For material parameters of crystals such as anthracene, the system has four surface states. In this case, it is worth stressing that there are two surface states strongly localized in the two first surface layers (first surface states) while the others behave like damped oscillatory states which have maximum absolute values of wave functions at the second surface layers (second surface states). This behavior is the main reason for the difference in the radiative decay rates of excitons in the first and the second surface layers, as will be presented in the context of the present paper.

Our paper is outlined as follows: In Sec. II we present the model of the considered MOQW's and the general solution of the difference equations in the SNLA. In Sec. III we make classifications of five classes of states in the SNLA. These classifications are useful to understand the energy scheme of excitons in MOQW's within the SNLA. In Sec. IV we present the method for determining the allowed states of the system. In this section the difference in the radiative decay rates of the first and second surface excitons is evaluated. Section V is the discussion part of the present paper.

II. MODEL AND GENERAL SOLUTION

A. Model

Consider a MOQW composed of $L=2N+1$ parallel infinite layers, with an 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 the layer.[18,21] Accordingly we take into account the first- and second-nearest-layer interactions. We further restrict ourselves to a symmetric system: there are two equivalent faces of MOQW's, each of which has two kinds of surface layers (the first and second surface layers).

The Hamiltonian of the system can be written as[12–15,20,22]

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

where $B_{n\vec{k}}(B^{\dagger}_{n\vec{k}})$ is the annihilation (creation) operator of a two-dimensional exciton in the nth layer with energy $E_n(\vec{k})$ and a two-dimensional wave vector $\vec{k}$, and M_{nm} is the matrix element for the transfer of excitation from the nth molecular layer to the mth one. In the NLA, M_{nm} has two equivalent contributions $R\delta_{m,n+1}$ and $R\delta_{m,n-1}$ regarded as the nearest-layer interaction. In the SNLA, it has four contributions, i.e., two of the nearest-layer interaction, and others, $S\delta_{m,n+2}$ and $S\delta_{m,n-2}$, which are equal to each other and regarded as the second-nearest-layer interaction. We then call R and S the nearest- and second-nearest-layer interactions, respectively. As we mentioned above, our system is symmetric with two equivalent first surface layers and two equivalent second surface layers; accordingly it can be assumed that $E_N=E_{-N}$ and $E_{N-1}=E_{-N+1}$. Here we count the layers of the system from $n=-N$ to $n=N$.

B. Difference equations and general solution

In the model considered, interlayer interactions are taken into account so that 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 we represent the eigenfunction of the whole system as

$$\Psi_{\vec{k}}=\sum_{n=-N}^{N}\varphi_n(\vec{k})B^{\dagger}_{n\vec{k}}|0\rangle,\quad(2)$$

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

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

is satisfied, with $\omega_{\vec{k}}$ the eigenenergy of the whole structure. Here and hereafter $\hbar=1$. Substitutions of Eqs. (1) and (2) into Eq. (3) within the SNLA produce the following difference equations for the eigenenergy ω and the envelope function of the eigenstate φ_n (the wave vector $\vec{k}$ of the motion in the layer planes is omitted for brevity from now on):

$$(\omega - E_0)\varphi_n = R(\varphi_{n+1} + \varphi_{n-1}) + S(\varphi_{n+2} + \varphi_{n-2}), \quad -N+1 < n < N-1, \tag{4}$$

$$(\omega - E_N)\varphi_N = R\varphi_{N-1} + S\varphi_{N-2}, \tag{5}$$

$$(\omega - E_{N-1})\varphi_{N-1} = R(\varphi_N + \varphi_{N-2}) + S\varphi_{N-3}, \tag{6}$$

$$(\omega - E_{-N})\varphi_{-N} = R\varphi_{-N+1} + S\varphi_{-N+2}, \tag{7}$$

$$(\omega - E_{-N+1})\varphi_{-N+1} = R(\varphi_{-N} + \varphi_{-N+2}) + S\varphi_{-N+3}, \tag{8}$$

where $E_0(\vec{k}) = E_n(\vec{k})$ for $-N+1 < n < N-1$ is the energy of $L-4$ internal layers. Here it should be noted that $E_n(\vec{k})$ is the energy of the exciton in nth layer without taking into account the transfer energy between layers. The solution of the difference equation (4) can be sought in the form

$$\varphi_n = x^n = \exp[i(p + i\gamma)nd], \tag{9}$$

where p and γ are real, and their allowed values are to be determined by using the boundary condition equations (5)–(8).

Inserting (9) into (4) we obtain the following equation for the eigenenergy:

$$\omega = E_0 + R(x + x^{-1}) + S(x^2 + x^{-2}). \tag{10}$$

Here, it is worth noting that, if x is the solution of Eq. (10) and has a complex form, then x^{-1}, x^*, and x^{*-1} also satisfy the equation and that the general solution is some linear combinations of x, x^{-1}, x^*, and x^{*-1}:

$$\varphi_n = Ax^n + Bx^{-n} + Cx^{*n} + Dx^{*-n}, \tag{11}$$

where A, B, C, and D are the coefficients and can be determined from the difference equations as well as the normalization condition of the wave functions.

Using (9), the equation for the eigenenergy (10) can be rewritten as

$$\begin{aligned}\omega - E_0 &= 2R\cos[(p+i\gamma)d] + 2S\cos[2(p+i\gamma)d] \\ &= 2R\cos(pd)\cosh(\gamma d) + 2S\cos(2pd)\cosh(2\gamma d) \\ &\quad - i\sin(pd)\sinh(\gamma d)[R + 4S\cos(pd)\cosh(\gamma d)].\end{aligned} \tag{12}$$

Here and hereafter $E_0 \equiv E_0(0)$ is taken as the energy reference. For a fixed value of ω, we have two pairs of (p,γ) satisfying Eq. (12) as long as S is finite. This is the first different point of the SNLA from the NLA. The dispersion relation $\omega(p,\gamma)$ of the exciton is obtained by coupling Eq. (12) with the boundary conditions Eqs. (5)–(8). Because ω, E_0, R, and S in our system are real quantities, the imaginary part on the right-hand side of Eq. (12) must vanish, leading to the following condition for one pair (p,γ):

$$\sin(p)\sinh(\gamma)[R + 4S\cos(p)\cosh(\gamma)] = 0. \tag{13}$$

Here, in (13) and hereafter we use p and γ in the unit of the interlayer spacing d.

Substitution of the general solution (11) into the difference equation (4) with the use of condition (13) leads to the following possibilities: (i) $p \neq 0$, $\gamma = 0$, and the eigenenegy is given by

$$\omega = E_0 + 2R\cos(p) + 2S\cos(2p); \tag{14}$$

(ii) $\gamma = 0$, $p = \pi j$ (j integer), and the eigenenergy is given by

$$\omega = E_0 + (-1)^j 2R\cosh(\gamma) + 2S\cosh(2\gamma); \tag{15}$$

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

$$\omega = E_0 + 2R\cos(p)\cosh(\gamma) + 2S\cos(2p)\cosh(2\gamma). \tag{16}$$

It is worth noting that case (iii) exists only in the SNLA, while cases (i) and (ii) are already known in the NLA.[20] However, here the situation is not the same as in the NLA, in which states belonging to cases (i) and (ii) are classified as band states and surface states, respectively. Now there are possibilities in which states originating from case (ii) must be classified as band states, and the situation becomes more complicated, as will be seen in Sec. III.

III. CLASSIFICATIONS OF BAND AND SURFACE STATES

We have two classes of band states and three classes of surface states depending upon the relative values of $R/4S$. In this section, classification of these states is discussed, and we will determine the eigenenergies and envelope functions of eigenstates of these surface states by using boundary condition equations (5)–(8) in Sec. III A.

A. Band states

States with energies given by Eq. (14) [case (i)] are also called band states as in the NLA. In the SNLA, however, there are two different classes of band states.

1. (p,p′)-band states

The eigenenergy from the case (i) has the extreme value $-(R^2+8S^2)/4S$ at $\cos(p) = -R/4S$ when $|R/4S| < 1$, and $2S(1+|R/S|)$ at $\cos(p) = \pm 1$. It can be proved that if $|R/4S| < 1$, the band energy in Eq. (14) extends over the following regions [region B1 in Figs. 1(a) and 1(b)]:

$$(E_0 - \Omega_m) < \omega \leqslant (E_0 - \Omega_1) \quad \text{if } S > 0, \tag{17}$$

$$(E_0 + \Omega_m) > \omega \geqslant (E_0 + \Omega_1) \quad \text{if } S < 0, \tag{18}$$

where $\Omega_m = (R^2 + 8S^2)/4|S|$ and $\Omega_1 = 2(|R| - |S|)$. Here there are two pure values of wave vectors p and p' corresponding to one value of energy ω, so that both functions $\cos(p)$ and $\cos(p')$ satisfy the eigenvalue equation (14). These two solutions $\cos(p)$ and $\cos(p')$ of the equation relate to each other by

$$\cos(p) + \cos(p') = -\frac{R}{2S}, \tag{19}$$

and the corresponding energy ω is given by

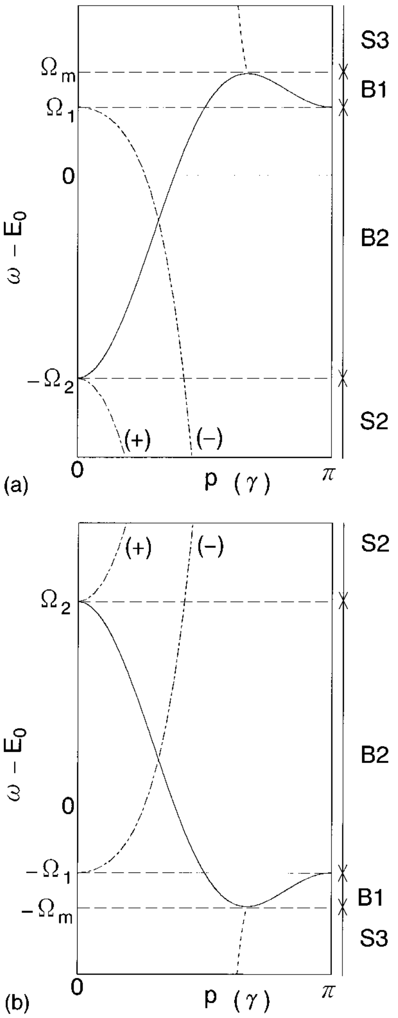

FIG. 1. Energy scheme of states with $|R/4S|<1$. (a) $R=-1.2$ cm^{-1} and $S=-0.6$ cm$^{-1}<0$. (b) $R=1.2$ cm^{-1} and $S=0.6$ cm$^{-1}>0$. Case (i) energy ω as a function of p, solid curve. Case (ii) ω as a function of γ, dashed-dotted curves. Curves $(+)$ and $(-)$ correspond to $(-1)^j\text{sign}(R)\text{sign}(S)=+1$ and -1, respectively. Case (iii) ω as a function of p, dashed curve.

$$\begin{aligned}\omega &= E_0+2R\cos(p)+2S\cos(2p)\\ &= E_0+2R\cos(p')+2S\cos(2p'). \qquad (20)\end{aligned}$$

In this case, these states are characterized by two real wave vectors p and p' which are determined in Sec. II B by using the boundary conditions (5)–(8) as well as relation (19). The envelope functions of eigenstates, therefore, take the general form

$$\varphi_n=A'\cos(np)+B'\sin(np)+C'\cos(np')+D'\sin(np'). \qquad (21)$$

We note at once that, because of the symmetry of the system, the eigenstates must be either symmetric $\varphi^s_{Bn}(p,p')$ or antisymmetric $\varphi^a_{Bn}(p,p')$. From Eq. (21) it can be easily proved that envelope functions of these eigenstates have the following forms:

$$\varphi^s_{Bn}(p,p')=A_1\cos(np)+A_1'\cos(np'), \qquad (22)$$

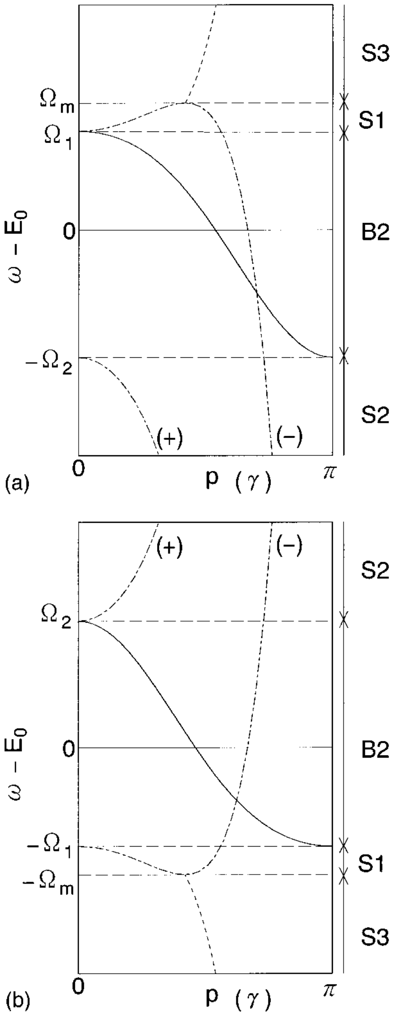

FIG. 2. Energy scheme of states with $|R/4S|>1$. (a) $R=-5$ cm^{-1} and $S=-0.625$ cm$^{-1}<0$. (b) $R=5$ cm^{-1} and $S=0.625$ cm$^{-1}>0$. Case (i) energy ω as a function of p, solid curve. Case (ii) ω as a function of γ, dashed-dotted curves. Curves $(+)$ and $(-)$ correspond to $(-1)^j\text{sign}(R)\text{sign}(S)=+1$ and -1, respectively. Case (iii) ω as a function of γ, dashed curve.

$$\varphi^a_{Bn}(p,p')=B_1\sin(np)+B_1'\sin(np'). \qquad (23)$$

These band states should be called the (p,p')-band states $[(p,p')$-BS$]$ in order to distinguish them from the other band states which may appear in the SNLA as below.

2. (p,γ)-band states

Considering case (ii), we can see that if $S=0$ (i.e., in the NLA) the energies given by Eq. (15) always go out of the levels of band energy given by Eq. (14), and, therefore, in the NLA, these states are classified as surface states. This also means that in the NLA, states belonging to case (ii) are always classified as surface states. In the SNLA, we have states with their energies given by Eq. (15) outside of the band energy, that are also called surface states. There are other possibilities that the corresponding states must be classified as band states. As can be seen clearly from Eq. (15) and also from Figs. 1 and 2 (regions $B2$ in these figures), if R and S have the same signs (opposite signs) and j is seclected so that $(-1)^j=-1(+1)$ or

$(-1)^j\mathrm{sign}(R)\mathrm{sign}(S)=-1$ (signs rule 1), where sign(R) and sign(S) are signs of R and S, respectively, there are the regions of energy ω given by Eq. (15), in which the states must be classified as band states. The energy regions of these band states are

$$(E_0-\Omega_1)<\omega\leqslant(E_0+\Omega_2) \quad \text{if } S>0, \tag{24}$$

$$(E_0-\Omega_2)<\omega\leqslant(E_0+\Omega_1) \quad \text{if } S<0, \tag{25}$$

where $\Omega_2=2(|R|+|S|)$. For the present class of (p,γ)-band states, one pair of (p,γ) comes from case (ii), i.e., $(\pi j,\gamma)$ with the energy $\omega=E_0+(-1)^j 2R\cosh(\gamma)+2S\cosh(2\gamma)$ and another pair of (p,γ) comes from case (i), i.e., $(p,0)$ with the energy $\omega=E_0+2R\cos(p)+2S\cos(2p)$, so that the eigenstate is described as a linear combination of these wave functions.

Analytically, in these regions we have

$$\begin{aligned}\omega&=E_0+2R\cos(p)+2S\cos(2p)\\&=E_0+(-1)^j2R\cosh(\gamma)+2S\cosh(2\gamma).\end{aligned} \tag{26}$$

It is clear from Eq. (26) that if p and γ correspond to one value of energy ω in the above regions, both functions cos(p) and $(-1)^j\cosh(\gamma)$ are to be the two solutions of the following equation:

$$4Sy^2+2Ry-(2S+\omega-E_0)=0; \tag{27}$$

therefore the relation between these two solutions is

$$\cos(p)+(-1)^j\cosh(\gamma)=-\frac{R}{2S}. \tag{28}$$

These band states should be called the (p,γ)-band states [(p,γ)-BS].

Note that the (p,p')-BS may appear if the condition $|R/4S|<1$ hold only, while the (p,γ)-BS may appear without any restriction of R and $S\neq 0$. Moreover, from (17) and (18) and (24) and (25) we can see that the energy regions of (p,p')-BS and (p,γ)-BS never overlap each other. Therefore, there are no situations in which the states belong to different classes of band states and correspond to one value of energy simultaneously.

In the case of (p,γ)-BS, the states are to be characterized by one pure real p, one pure imaginary value $i\gamma$ of wave vectors, and one integer value j. This may be called a quasilocalized state embedded in the continuum spectrum of the band energy. The envelope functions of the symmetric and antisymmetric eigenstates have the following forms:

$$\varphi^s_{Bn}(p,\gamma)=A_2\cos(np)+A_2'(-1)^{nj}\cosh(n\gamma), \tag{29}$$

$$\varphi^a_{Bn}(p,\gamma)=B_2\sin(np)+B_2'(-1)^{nj}\sinh(n\gamma). \tag{30}$$

B. Surface states

Let us pay attention to case (ii) again. Schematically, the energy function ω in Eq. (15) corresponds to states belonging to three different classes of states. The first corresponds to energy regions given by (24) and (25), which are classified as (p,γ)-BS. The others belong to surface states as below. In this subsection, we discuss states originating from the energy equations of Eqs. (15) and (16). The eigenenergies will be determined in Sec. III B 1 by using the boundary conditions Eqs. (5)–(8).

1. $(\gamma j,\gamma' j)$-*surface states*

It can be proved that if the condition $|R/4S|>1$ and $(-1)^j\mathrm{sign}(R)\mathrm{sign}(S)=-1$ (signs rule 1) are satisfied, the function ω given by Eq. (15) has extreme value $-(R^2+8S^2)/4S$ at $\cosh(\gamma)=-(-1)^jR/4S$. In this case the energy function has regions in which, corresponding to one value of energy ω, there are two values γ and γ' with the same value j. The energy regions of these states [regions $S1$ in Figs. 2(a) and 2(b)] are

$$(E_0-\Omega_m)<\omega<(E_0-\Omega_1) \quad \text{if } S>0, \tag{31}$$

$$(E_0+\Omega_1)<\omega<(E_0+\Omega_m) \quad \text{if } S<0. \tag{32}$$

In these regions, both functions cosh(γ) and cosh(γ') are solutions of Eq. (15); therefore we have a relation

$$\cosh(\gamma)+\cosh(\gamma')=-\frac{(-1)^jR}{2S}, \tag{33}$$

where j is selected to satisfy condition $(-1)^j\mathrm{sign}(R)\ \mathrm{sign}(S)=-1$ (signs rule 1). In these regions, the energies of the surface states are given by

$$\begin{aligned}\omega&=E_0+(-1)^j2R\cosh(\gamma)+2S\cosh(2\gamma)\\&=E_0+(-1)^j2R\cosh(\gamma')+2S\cosh(2\gamma').\end{aligned} \tag{34}$$

These surface states are characterized by two pure imaginary values $i\gamma$ and $i\gamma'$ of wave vectors and an integer j. The envelope functions of the symmetric and antisymmetric eigenstates take the forms

$$\varphi^s_{Sn}(\gamma j,\gamma' j)=(-1)^{nj}[A_2\cosh(n\gamma)+A_2'\cosh(n\gamma')], \tag{35}$$

$$\varphi^a_{Sn}(\gamma j,\gamma' j)=(-1)^{nj}[B_2\sinh(n\gamma)+B_2'\sinh(n\gamma')]. \tag{36}$$

These surface states should be classified as $(\gamma j,\gamma' j)$-surface states [$(\gamma j,\gamma' j)$-SS] in order to distinguish them from the other classes of surface states.

Note that for the energy regions of $(\gamma j,\gamma' j)$-SS [Eqs. (31) and (32)], corresponding to one value of energy, there are two different values of γ and γ' with the same integer value j. The energy regions of the $(\gamma j,\gamma' j)$-SS appear if the condition $|R/4S|>1$ and the signs rule 1 are fulfilled. On the other hand, the energy ω in Eq. (15) with a given sign value of the expression $(-1)^j$ (both values $+1$ and -1) is monotonic function with respect to γ except in the above regions of $(\gamma j,\gamma' j)$-SS [regions $S1$ in Figs. 2(a) and 2(b)]. However, it also has other regions without restriction of R and $S\neq 0$ in which there are two pairs γ,j and γ',j', with j and j' satisfying condition $(-1)^j(-1)^{j'}=-1$, corresponding to one value of energy as can be seen below.

2. $(\gamma j,\gamma' j')$-surface states

It can be proved from Eq. (15) and more clearly from Figs. 1 and 2 that the energy in the regions (regions $S2$ in these figures)

$$\omega>(E_0+\Omega_2) \quad \text{if } S>0, \tag{37}$$

$$\omega<(E_0-\Omega_2) \quad \text{if } S<0 \tag{38}$$

goes out of the band levels, and therefore the corresponding states are classified as surface states.

In these regions, corresponding to one value of energy ω, there are two pairs γ,j and γ',j' which satisfy the eigenenergy equation (15). In this case, generally we have

$$\begin{aligned}\omega&=E_0+(-1)^j 2R\cosh(\gamma)+2S\cosh(2\gamma)\\&=E_0+(-1)^{j'}2R\cosh(\gamma')+2S\cosh(2\gamma').\end{aligned} \tag{39}$$

From Eq. (39) we have the following relation:

$$(-1)^j\cosh(\gamma)+(-1)^{j'}\cosh(\gamma')=-\frac{R}{2S}. \tag{40}$$

It is clear that if $(-1)^j=(-1)^{j'}$ then Eq. (40) becomes relation (33) obtained above, which is valid only if the condition $|R/4S|>1$ and $(-1)^j\mathrm{sign}(R)\mathrm{sign}(S)=-1$ are satisfied. In this case, as clearly presented in Sec. III B 1 the energy regions are given by (31) and (32), and the corresponding states are classified as $(\gamma j,\gamma' j)$-SS. Therefore, if the two pairs γ,j and γ',j' correspond to one value of energy in the regions given by (37) and (38), then the values of j and j' must satisfy condition $(-1)^j(-1)^{j'}=-1$ (signs rule 2). In this case, these states are characterized by two pairs γ,j and γ',j', and should be classified as $(\gamma j,\gamma' j')$-surface states $[(\gamma j,\gamma' j')$-SS].

The envelope functions of the symmetric and antisymmetric eigenstates of the $(\gamma j,\gamma' j')$-SS can be proved to have the following forms:

$$\varphi^s_{Sn}(\gamma j,\gamma' j')=A_4(-1)^{nj}\cosh(n\gamma)+A_4'(-1)^{nj'}\cosh(n\gamma'), \tag{41}$$

$$\varphi^a_{Sn}(\gamma j,\gamma' j')=B_4(-1)^{nj}\sinh(n\gamma)+B_4'(-1)^{nj'}\sinh(n\gamma'). \tag{42}$$

Note that the $(\gamma j,\gamma' j')$-SS may appear without any restriction of R and $S\neq 0$, while the $(\gamma j,\gamma' j)$-SS may appear only if the condition $|R/4S|>1$ holds. This means that for $|R/4S|>1$ there may be two different classes of surface states also originating from case (ii).

3. (p,γ)-surface states

For case (iii), the eigenenergy is given by Eq. (16)

$$\omega=E_0+2R\cos(p)\cosh(\gamma)+2S\cos(2p)\cosh(2\gamma),$$

and the following relation comes from condition (13):

$$\cos(p)=-\frac{R}{4S\cosh(\gamma)}. \tag{43}$$

It can be easily proved from Eq. (16) and clearly seen from Figs. 1 and 2 that the regions of the energy function ω given by Eq. (16) are (regions $S3$ in these figures):

$$\omega<(E_0-\Omega_m) \quad \text{if } S>0, \tag{44}$$

$$\omega>(E_0+\Omega_m) \quad \text{if } S<0. \tag{45}$$

Therefore, states belonging to case (iii) are classified as surface states because their energies always go out of the band energy.

In this case, these surface states are characterized by complex values $(p\pm i\gamma)$ of wave vectors, and therefore should be classified as (p,γ)-surface states $[(p,\gamma)$-SS]. The symmetric and antisymmetric eigenstates are of the forms

$$\begin{aligned}\varphi^s_{Sn}(p,\gamma)&=A_5\cos[(p+i\gamma)n]+A_5'\cos[(p-i\gamma)n]\\&=(A_5+A_5')\cos(np)\cosh(n\gamma)\\&\quad+i(A_5'-A_5)\sin(np)\sinh(n\gamma),\end{aligned} \tag{46}$$

$$\begin{aligned}\varphi^a_{Sn}(p,\gamma)&=B_5\sin[(p+i\gamma)n]+B_5'\sin[(p-i\gamma)n]\\&=(B_5+B_5')\sin(np)\cosh(n\gamma)\\&\quad+i(B_5-B_5')\cos(np)\sinh(n\gamma).\end{aligned} \tag{47}$$

Note that Ω_m in (17) and (18), (31) and (32), and (44) and (45) has the same formula $(R^2+8S^2)/4|S|$ but different meanings. In (17) and (18), Ω_m is the extreme value of function $(\omega-E_0)$ in Eq. (14) if the condition $|R/4S|<1$ holds, while in (31) and (32) it is the extreme value of function $(\omega-E_0)$ given by (15) with $|R/4S|>1$. In (44) and (45), $\Omega_m(-\Omega_m)$ is the minimum (maximum) of function $(\omega-E_0)$ given by Eq. (16) if $S<0$ $(S>0)$ with any values of R and $S\neq 0$. It is clear that the energy regions of the different classes of states do not overlap each other.

C. Some remarks

(1) In the SNLA, there are two classes of band states (p,p)-BS, and (p,γ)-BS, and three classes of surface states $(\gamma j,\gamma' j')$-SS, $(\gamma j,\gamma' j)$-SS, and (p,γ)-SS. It is worth noticing that, in any case, there are no situations in which, corresponding to one value of energy, there are states which belong to different classes of states.

(2) The case which was discussed by Mahan and Obermair[18] is nothing other than the (p,p')-BS presented above. As can be seen in Sec. III A 1, these band states may appear if the condition $|R/4S|<1$ is satisfied. In Ref. 18 the authors gave several typical values of R and S [$v(1)$ and $v(2)$ in this paper], and the values of $|R/4S|$ are typically larger than 2. It is clear from the results in Sec. III A that, if we consider only (p,p')-BS in the SNLA as in Ref. 18, we do not have enough information about the band states of system. In principle, these band states may appear only if $|R/4S|<1$.

(3) The SNLA had also been discussed by Koster and Slater.[17] In their paper, Koster and Slater predicted that there are only two classes of surface states, one characterized by two pure imaginary values $[(\gamma,\gamma')$-surface states], and the other characterized by one complex value of wave vectors

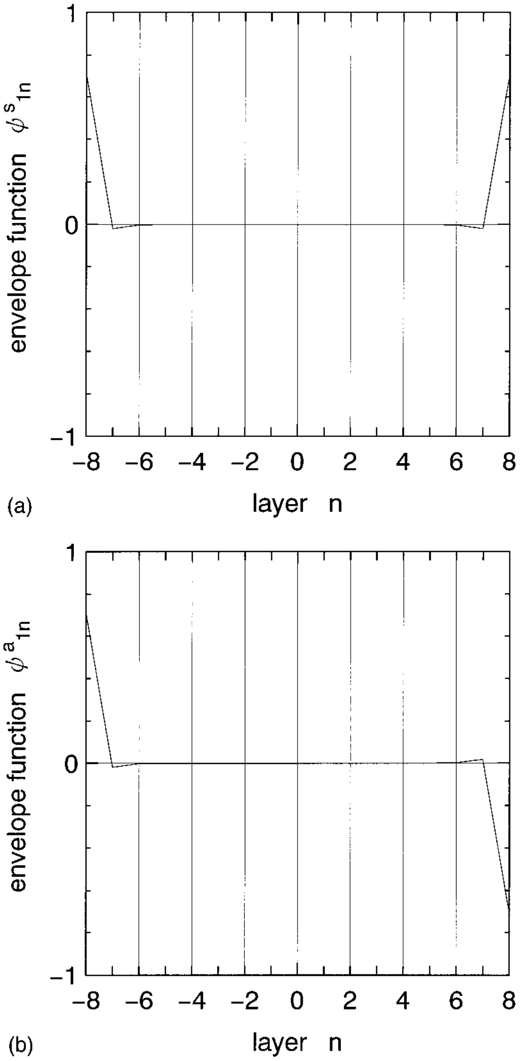

FIG. 3. Behavior of the envelope function of the first surface states with $S=-0.625\ \mathrm{cm}^{-1}$, $R=-5\ \mathrm{cm}^{-1}$, $\Delta_1=-204\ \mathrm{cm}^{-1}$, and $\Delta_2=-6\ \mathrm{cm}^{-1}$. (a) For the symmetric state. (b) For the antisymmetric state.

$[(p,\gamma)$-surface states]. However, as presented in Sec. III B, there are three classes of surface states, and in the cases of two classes, $(\gamma j,\gamma' j')$-SS and $(\gamma j,\gamma' j)$-SS, besides two purely 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 values of integer j (and j') play an important role. The surface states of these two classes cannot be formed if signs rules 1 and 2 are not taken into account. Here it is worth mentioning that, in the SNLA, the state at a given energy is described by two wave vectors rather than just one as in the NLA (for more details see Ref. 18). Another argument of Koster and Slater is that they predicted that energy levels of states belonging to (γ,γ')- and (p,γ)-surface states always locate on opposite sides of the band energy. This means that, if energy levels of (γ,γ')-surface states are above the top of band energy, then the energies of (p,γ)-surface states are below the bottom of band energy, and vice versa (see Fig. 3 in Ref. 17). As presented in Sec. III B, if $|R/4S|<1$ the $(\gamma j,\gamma' j')$-SS and (p,γ)-SS are on opposite sides of the band states; but if $|R/4S|>1$, the energy levels of $(\gamma j,\gamma' j)$-SS and (p,γ)-SS are on the same side, but on different sides from the $(\gamma j,\gamma' j')$-SS. In fact, the arguments of the authors in Ref. 17 were formally based on our eigenenergy equation Eq. (14). They had no concrete conditions such as Eq. (13) as in the present paper.

All the above conclusions are based on the energy scheme and eigenvalue equations (14)–(16). However, the number of states belonging to each class and the allowed values of states, i.e., (p,γ) defined in Eq. (9) [or the values of (p,p'), (p,γ), $(\gamma j,\gamma' j)$, and $(\gamma j,\gamma' j')$ depending on the class of the states] are to be determined by using the boundary condition equations (5)–(8) (called the special equations). At the same time, the eigenenergies of the exciton are determined by putting the allowed values of states into Eqs. (14)–(16). In Sec. IV the method to determine the allowed states, i.e., the eigenenergies of the system, is presented. Attention is to be paid to the surface states, and to the difference in radiative decay rates of the first and second surface excitons.

IV. FIRST AND SECOND SURFACE EXCITONS

A. Determinations of allowed states

Substituting of the envelope functions of eigenstates obtained in Sec. III into the boundary condition equations (5)–(8), we obtain equations which can determine the allowed values of states of our system (called state equations). For each allowed state, there are six quantities which must be determined, i.e., two coefficients A_i, A_i' or B_i, B_i' (i from 1 to 5) for each envelope function of eigenstates, and two allowed pairs (p,γ) which determine the eigenenergy. Condition (13) and the signs rules 1 and 2 reduce these six quantities to four. On the other hand, as two pairs of special equations, i.e., the boundary conditions (5) and (6) and (7) and (8), are equivalent in our symmetric system, we have two independent boundary conditions. In addition, we have one relation between two solutions of eigenenergy equations for each class of states, e.g., Eqs. (19), (28), (33), (40), or (43), and one normalization condition for the wave functions. Therefore, it is sufficient to determine the allowed states of the system. In principle, the general method for determining the allowed values of state is the same for all classes of states. However, for each class of states we have one distinguished kind of state equation, including one equation for symmetric and another for antisymmetric states. In the following subsections we will derivate state equations for the (p,γ)-SS, as an example.

1. Equations for symmetric states

In this subsection, as an example, we present the derivation of the state equation for symmetric states of (p,γ)-SS. Substitution of Eq. (46) into the special equations (5) and (6) or (7) and (8), we have the following equations:

$$\begin{aligned} &A_5\{\Delta_1\cos[N(p+i\gamma)]+R\cos[(N+1)(p+i\gamma)] \\ &\quad +S\cos[(N+2)(p+i\gamma)]\} \\ &= -A_5'\{\Delta_1\cos[N(p-i\gamma)]+R\cos[(N+1)(p-i\gamma)] \\ &\quad +S\cos[(N+2)(p-i\gamma)]\} \end{aligned} \tag{48}$$

and

$$A_5\{\Delta_2\cos[(N-1)(p+i\gamma)]+S\ \cos[(N+1)(p+i\gamma)]\}$$
$$=-A_5'\{\Delta_2\cos[(N-1)(p-i\gamma)]$$
$$+S\ \cos[(N+1)(p-i\gamma)]\}, \tag{49}$$

where, $\Delta_1=E_0-E_N$ and $\Delta_2=E_0-E_{N-1}$.

Eliminating A_5 and A_5' from the above equations, we arrive at an equation which has a complex form:

$$(a+ib)(c-id)=(a-ib)(c+id), \tag{50}$$

where a, b, c, and d are real expressions obtained from Eqs. (48) and (49). From Eq. (50) we obtain an equation of the form $ad=bc$ which is the state equation for the symmetric states of (p,γ)-SS. The left-hand side of the equation is as follows:

$$\{\Delta_1\cos(Np)\cosh(N\gamma)+R\ \cos[(N+1)p]\cosh[(N+1)\gamma]$$
$$+S\ \cos[(N+2)p]\cosh[(N+2)\gamma]\}$$
$$\times\{\Delta_2\sin[(N-1)p]\sinh[(N-1)\gamma]$$
$$+S\ \sin[(N+1)p]\sinh[(N+1)\gamma]\}, \tag{51}$$

and the right-hand side is

$$\{\Delta_1\sin(Np)\sinh(N\gamma)+R\ \sin[(N+1)p]\sinh[(N+1)\gamma]$$
$$+S\ \sin[(N+2)p]\sinh[(N+2)\gamma]\}$$
$$\times\{\Delta_2\cos[(N-1)p]\cosh[(N-1)\gamma]$$
$$+S\ \cos[(N+1)p]\cosh[(N+1)\gamma]\}. \tag{52}$$

Combining Eqs. (51) and (52) and relation (43), we can determine graphically the allowed values of p and γ of the states. Special equations (48) and (49), along with the normalization requirement on Ψ, are sufficient to determine coefficients A_5 and A_5'. The eigenenergies $\omega(p,\gamma)$ are obtained by inserting the allowed values of p and γ into Eq. (16).

2. Equations for antisymmetric states

By the same method as presented above, we obtain another state equation for antisymmetric states of (p,γ)-SS, with the left-hand side of the equation having the form

$$\{\Delta_1\sin(Np)\cosh(N\gamma)+R\ \sin[(N+1)p]\cosh[(N+1)\gamma]$$
$$+S\ \sin[(N+2)p]\cosh[(N+2)\gamma]\}$$
$$\times\{\Delta_2\cos[(N-1)p]\sinh[(N-1)\gamma]$$
$$+S\ \cos[(N+1)p]\sinh[(N+1)\gamma]\}, \tag{53}$$

and the right-hand side

$$\{\Delta_1\cos(Np)\sinh(N\gamma)+R\ \cos[(N+1)p]\sinh[(N+1)\gamma]$$
$$+S\ \cos[(N+2)p]\sinh[(N+2)\gamma]\}$$
$$\times\{\Delta_2\sin[(N-1)p]\cosh[(N-1)\gamma]$$
$$+S\ \sin[(N+1)p]\cosh[(N+1)\gamma]\}. \tag{54}$$

Combining Eqs. (53) and (54) and relation (43), we can determine the allowed values of p and γ of the states graphically. The coefficients B_5 and B_5' are also determined in the same way as in the case of symmetric states.

3. Number of states

By the same method as presented in Secs. IV A 1 and IV A 2, we can establish state equations to determine the allowed values of all classes of states, and solve them graphically. Carefully considering all these classes, we obtain some conclusions about the number of states as well as their characteristics depending not only on the absolute values of parameters Δ_1, Δ_2, R, and S, but also on the signs of these quantities as follows.

(a) $|R|>|\Delta_1|$: no surface states, and number of band states = $L\equiv 2N+1$. $|R/4S|>1$, L states of (p,γ)-BS; $|R/4S|<1$, L states of (p,p')-BS and (p,γ)-BS.

(b) $|\Delta_2|<|R|<|\Delta_1|$: two surface states, and $(L-2)$ band states. $\text{sign}(S)=\text{sign}(\Delta_1)$, two states of $(\gamma j,\gamma' j)$-SS or two states of (p,γ)-SS: (i) if $S>0$, energies of the surface states lie below the botom of the band energy; (ii) if $S<0$, energies of the surface states lie above the top of the band energy. $\text{sign}(S)=-\text{sign}(\Delta_1)$, two states of $(\gamma j,\gamma' j')$-SS: (i) if $S>0$, energies of the surface states lie above the top of the band energy; (ii) if $S<0$, energies of the surface states lie below the botom of the band energy.

(c) $|R|<|\Delta_2|<|\Delta_1|$: four surface states, and $(L-4)$ band states. $\text{sign}(S)=\text{sign}(\Delta_1)$, four states of (p,γ)-SS and $(\gamma j,\gamma' j)$-SS: (i) if $S>0$, energies of the surface states lie below the botom of the band energy; (ii) if $S<0$, energies of the surface states lie above the top of the band energy. $\text{sign}(S)=-\text{sign}(\Delta_1)$, four states of $(\gamma j,\gamma' j')$-SS: (i) if $S>0$, energies of the surface states lie above the top of the band energy; (ii) if $S<0$, energies of the surface states lie below the botom of the band energy.

It is worth noting that the total number of states is the same as in the nearest-layer approximation, but the number of surface states can be changed importantly depending upon the material constants. Now we have a condition for the appearance of at most four surface states. 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 levels comparing with the band levels. In solving the state equations (51)–(54) graphically, trivial and unphysical solutions such as $\gamma=0$, $p=0$, or π are excluded. When the system has only two surface states, these states are strongly localized in the first surface layers. In this case the physics is the same as in the NLA. The additional effect comes from the case in which the system has four surface states. As presented above, the condition for that case is $|\Delta_1|>|\Delta_2|>|R|$. In Sec. IV B, we will investigate the behavior of four surface states, and evaluate the different radiative decay rates of the first and second surface excitons.

B. First and second surface excitons

Let us now consider the case in which the system has four surface states. The conditions for that case is $|\Delta_1|>|\Delta_2|>|R|$. Solving the state equations for all three kinds of surface states with various values of Δ_1, Δ_2, R, and

S, we have the following possibilities: (a) four states of $(\gamma j,\gamma' j')$-SS, (b) four states of (p,γ)-SS, (c) four states of $(\gamma j,\gamma' j)$-SS, and (d) two states of (p,γ)-SS and two states of $(\gamma j,\gamma' j)$-SS.

Among four surface states, there are two states (one symmetric and another antisymmetric) belonging to the same class of states and having the same energy, which can be regarded as first surface states, and the other two (one symmetric and one antisymmetric), belonging to one class of states and having the same energy, regarded as second surface states. The first states have energies higher (lower) than the second ones if the surface levels are above (below) the top (botom) of the band energy. It should be noted that the twofold degeneracy of the surface states is due to the symmetry of the system under consideration. The first and second surface states may belong to one class of states [cases (a), (b), and (c)], but they may also belong to two different classes [case (d)], i.e., the classification $|R|<|\Delta_2|<|\Delta_1|$ and $S<0$ with $\Delta_1<0$. In case (d), the first surface states belong to (p,γ)-SS and the second ones belong to $(\gamma j,\gamma' j)$-SS.

Once we obtain the allowed values of states, we can obtain the eigenenergies by Eqs. (14)–(16), and then use the special equations and the nomalization requirement $|\Psi|^2=\Sigma_{n=-N}^{N}|\varphi_n^{a,s}|^2=1$ to determine coefficients A_i,A_i' or B_i,B_i', i.e., envelope functions of eigenstates of all classes are determined. The behavior of the first and second surface states is described in Figs. 3 and 4 with the parameters chosen as $\Delta_1=-204\ \mathrm{cm}^{-1}$, $\Delta_2=-6\ \mathrm{cm}^{-1}$, $R=-5\ \mathrm{cm}^{-1}$, and $S=-0.625\ \mathrm{cm}^{-1}$. These values may correspond to anthracene crystal, as will be discussed below. As can be clearly seen from these figures, the first surface states [in this case belonging to (p,γ)-SS] are strongly localized in the first surface layers, and the amplitude of the envelope function is very small at the second surface layers, and nearly equal to zero in all the whole system. The envelope function of the second states [in this case the $(\gamma j,\gamma' j)$-SS] behaves as a damped oscillation. It is nearly equal to zero at the first surface layer, shows a maximum amplitude at the second one, and is damped oscillating into deeper layers of the system. If the number of layers of the system is large enough, the envelope function of the second states are nearly equal to zero in the middle part of the system. The behavior of the first and second surface states described above is very meaningful to understanding why the first and second surface excitons shows different radiative decay rates. One can see that the first excitonic surface states are strongly localized at the first surface layer, and nearly vanish over the other part of the system. Therefore these states can radiatively decay, emitting a radiation field outside the system with large oscillator strength due to a coherent superposition of the transition dipole moments at each layer. The second states are less radiative than the first ones because the oscillating behavior of the envelope function partially cancels out the transition dipole moment of each layer.

As the first problem which can be addressed in terms of the envelope functions of eigenstates of excitonic surface states, we will show the reason for the quite different radiative decay rates of the first and second surface excitons, which were observed by Aaviksoo, Lippmaa, and Reinot.[6] We choose material constants corresponding to anthracene crystal:[6,12] $\Delta_1=E_0-E_N=-204\ \mathrm{cm}^{-1}$ and $\Delta_2=E_0-E_{N-1}=-6\ \mathrm{cm}^{-1}$. We have no observed data for R and S, and estimate these by using the numerical results of Philpott[21] for dipolar interaction between the (001) layers of anthracene. The relative magnitudes of the nearest layers R and the second-nearest layers S dipolar interactions, as well as the signs of R and S, depend on the direction of transition dipole moments. Therefore we choose several combinations of R and S as follows: (R,S) = $(\pm 2\ \mathrm{cm}^{-1},\pm 0.2\ \mathrm{cm}^{-1})$, $(\pm 2\ \mathrm{cm}^{-1},\pm 0.02\ \mathrm{cm}^{-1})$, $(\pm 5\ \mathrm{cm}^{-1},\pm 0.5\ \mathrm{cm}^{-1})$, and $(\pm 5\ \mathrm{cm}^{-1},\pm 0.625\ \mathrm{cm}^{-1})$. Then the discussion of the present section is applicable to this system, resulting in four surface states. When the number of layers is larger than six, we are free from a delicate finite-size effect of the number of surface states.[20] Furthermore, for a number of layers larger than 10, the symmetric and antisymmetric states are degenerate in energy, and the two surfaces are almost independent. We are now able to evaluate the radiative decay rates for the α state of the exciton in terms of the electric dipole moment of the total system:

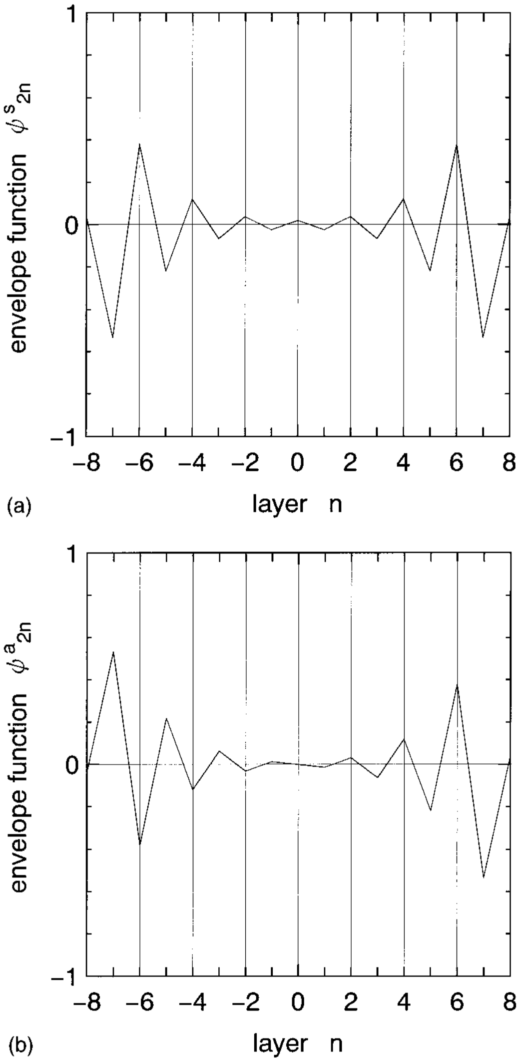

FIG. 4. Behavior of the envelope function of the second surface states with $S=-0.625\ \mathrm{cm}^{-1}$, $R=-5\ \mathrm{cm}^{-1}$, $\Delta_1=-204\ \mathrm{cm}^{-1}$, and $\Delta_2=-6\ \mathrm{cm}^{-1}$. (a) For the symmetric state. (b) For the antisymmetric state.

TABLE I. Relative magnitude of radiative decay rates Γ_1/Γ_2 and energy differences δ_1 and δ_2 depending on (R,S), with $\Delta_1=-204\ \mathrm{cm}^{-1}$, $\Delta_2=-6\ \mathrm{cm}^{-1}$, and $\mathrm{sign}(R)=\mathrm{sign}(S)$.

R (cm^{-1})	S (cm^{-1})	Class of 1st SS	Class of 2nd SS	δ_1 (cm^{-1})	δ_2 (cm^{-1})	$\Gamma_1/\Gamma 2$
$+2$	$+0.2$	$(\gamma j,\gamma' j')$-SS	$(\gamma j,\gamma' j')$-SS	204.02	6.61	1.94
$+2$	$+0.02$	$(\gamma j,\gamma' j')$-SS	$(\gamma j,\gamma' j')$-SS	204.01	6.59	1.78
-2	-0.2	(p,γ)-SS	(p,γ)-SS	204.02	6.61	1.94
-2	-0.02	(p,γ)-SS	$(\gamma j,\gamma' j)$-SS	204.01	6.59	1.78
$+5$	$+0.625$	$(\gamma j,\gamma' j')$-SS	$(\gamma j,\gamma' j')$-SS	204.14	9.45	7.6
-5	-0.625	(p,γ)-SS	$(\gamma j,\gamma' j)$-SS	204.14	9.45	7.6

$$\vec{P}_\alpha=\sum_{n=-N}^{N}\vec{\mu}\varphi_{\alpha,n}, \tag{55}$$

and the eigenfunctions obtained in this section describe the envelope functions analytically. The transition dipole moment $\vec{\mu}$ per unit layer depends on the wave vector in the plane and the coherent range of the excitation in the plane. Here, however, we assumed the constant $\vec{\mu}$ both for the first and second surface excitons and for each layer because the radiative decay of the exciton with in-plane wave vector nearly equal to zero is dominant. Then the relative magnitude of the radiative decay rates is evaluated only in terms of the envelope function of the first and the second surface excitons $\varphi_{1,n}$ and $\varphi_{2,n}$, as follows:

$$\frac{\Gamma_1}{\Gamma_2}\approx\frac{|\vec{P}_1|^2}{|\vec{P}_2|^2}=\frac{|\Sigma_{n=-N}^{N}\varphi_{1,n}|^2}{|\Sigma_{n=-N}^{N}\varphi_{2,n}|^2}. \tag{56}$$

Here Γ_1 and Γ_2 are the radiative decay rates of the first and second surface excitons, respectively. From Eq. (56) one can see that there are only contributions of two symmetric states in radiative decay rates among the four surface states. The characteristics of the first and second surface states are numerically studied with the use of the material constants as $\Delta_1\equiv E_0-E_N=-204\ \mathrm{cm}^{-1}$ and $\Delta_2\equiv E_0-E_{N-1}=-6\ \mathrm{cm}^{-1}$, and several combinations of R and S having the same signs and opposite signs are given in Tables I and II, respectively. One can see from Table I [i.e., $\mathrm{sign}(R)=\mathrm{sign}(S)$] that the energy differences $\delta_1\equiv\omega_1-E_0$ and $\delta_2\equiv\omega_2-E_0$, ($\omega_1$ and ω_2 are the energies of the first and second surface states, respectively), as well as the relative magnitude of the radiative decay rates, are not sensitive to the value of S, but that these quantities depend importantly on $|R|$. For example, with the fixed value $R=-2\ \mathrm{cm}^{-1}$, for $S=-0.2\ \mathrm{cm}^{-1}$ we obtain $p_1=1.7278$ and $\gamma_1=3.4637$ for the first surface states [in this case (p,γ)-SS] giving $\delta_1=204.02\ \mathrm{cm}^{-1}$, $p_2=2.6567$ and $\gamma_2=1.6990$, giving $\delta_2=6.61\ \mathrm{cm}^{-1}$, for the second surface states $[(p,\gamma)$-SS]; and $\Gamma_1/\Gamma_2=1.95$. For $S=-0.02\ \mathrm{cm}^{-1}$ with others fixed, we obtain $p=2.0886$ and $\gamma=4.615$ for the first surface states $[(p,\gamma)$-SS], giving $\delta_1=204.019\ \mathrm{cm}^{-1}$; $\gamma=1.1193$ and $\gamma'=4.5706$, giving $\delta_2=6.59\ \mathrm{cm}^{-1}$, for the second surface states $[(\gamma j,\gamma' j)$-SS]; and $\Gamma_1/\Gamma_2=1.78$. If we increase the value of $|R|$, the results change importantly. For example, with $R=-5\ \mathrm{cm}^{-1}$ and $S=-0.625\ \mathrm{cm}^{-1}$, we obtain $p=1.793\,35$ and $\gamma=2.8941$ for the first surface states $[(p,\gamma)$-SS], giving $\delta_1=204.14\ \mathrm{cm}^{-1}$; $\gamma=0.535\,17$ and $\gamma'=1.7094$, giving $\delta_2=9.45\ \mathrm{cm}^{-1}$ for the second surface states $[(\gamma j,\gamma' j)$-SS], and $\Gamma_1/\Gamma_2=7.6$ (the change of S leads to an unimportant change in results). As already mentioned above, the values $\delta_1=213\pm1\ \mathrm{cm}^{-1}$ and $\delta_2=10.2\pm0.2\ \mathrm{cm}^{-1}$ were observed by Nozue, Kawaharada, and Goto,[19] and the difference in the radiative decay rates $\Gamma_1/\Gamma_2\sim8$ was observed by Aaviksoo, Lippmaa, and Reinot.[6] From Table I, one can see that if $|R|=2\ \mathrm{cm}^{-1}$ the results are different from the experimental observations Refs. 6 and 19. These differences become smaller than that if the calculations are carried out with $|R|=3$ and $4\ \mathrm{cm}^{-1}$ (the results are not shown in Table I as this is not necessary). However, if $\mathrm{sign}(R)=-\mathrm{sign}(S)$, the results in Table II show that the radiative decay rate of the second surface exciton becomes larger than that of the first one. This is because the magnitude of the envelope function of the second surface state in this case, i.e., $\mathrm{sign}(R)=-\mathrm{sign}(S)$, is not a damped oscillation but one that extends over a few layers with the same sign. These results for the case $\mathrm{sign}(R)=-\mathrm{sign}(S)$ given in Table II [with $\mathrm{sign}(\Delta_1)=\mathrm{sign}(\Delta_2)$] are not only unphysical but also contrary to the experimental observations.

Finally we evaluate the absolute values of the radiative lifetime for the first and second surface excitons. The transition dipolemoment $\vec{\mu}$ per unit layer depends on the coherent length $L^*=\sqrt{2\pi\hbar/\Gamma M}$ of the two-dimensional exciton,[23] where Γ is its spectrum half-width and M its effective mass. The radiative decay rates Γ_1 and Γ_2 for the first and second surface excitons are evaluated by

TABLE II. Relative magnitude of radiative decay rates Γ_1/Γ_2 and energy differences δ_1 and δ_2 depending on (R,S), with $\Delta_1=-204\ \mathrm{cm}^{-1}$, $\Delta_2=-6\ \mathrm{cm}^{-1}$, and $\mathrm{sign}(R)=-\mathrm{sign}(S)$.

R (cm^{-1})	S (cm^{-1})	Class of 1st SS	Class of 2nd SS	δ_1 (cm^{-1})	δ_2 (cm^{-1})	$\Gamma_1/\Gamma 2$
-2	$+0.2$	$(\gamma j,\gamma' j')$-SS	$(\gamma j,\gamma' j')$-SS	204.22	6.61	0.575
-2	$+0.02$	$(\gamma j,\gamma' j')$-SS	$(\gamma j,\gamma' j')$-SS	204.01	6.59	0.505
$+2$	-0.2	(p,γ)-SS	(p,γ)-SS	204.02	6.61	0.575
$+2$	-0.02	(p,γ)-SS	$(\gamma j,\gamma' j)$-SS	204.01	6.59	0.505

$$\Gamma_i=\Gamma_0(L^*/u)^2\left|\sum_{n=-N}^{N}\phi_{i,n}\right|^2, \tag{57}$$

for $i=1$ and 2, where $\Gamma_0=2\times10^8$ sec^{-1} is the radiative decay rate of a single molecule and u the size of a unit cell. The lifetimes $T_1=1/\Gamma_1$ and $T_2=1/\Gamma_2$ are estimated to be on the order of 1 and 10 ps, respectively. Here we evaluated L^* to be 700 Å by using $\Gamma=10^{12}$ sec^{-1}, and $M=10^{-27}$ g, and used the size of unit cell $u=7$ Å. We neglected the nonradiative channels, and this looks to be justified because the observed dephasing rate[7] is of the same order of magnitude as the estimated radiative decay rate for the first surface exciton.

V. DISCUSSION

In the present paper, we have developed a theory of excitonic surface states in multilayer organic quantum wells in the framework of the second-nearest-layer approximation. For the first time, to our knowledge, two classes of band states (p,p)-BS and (p,γ)-BS and three classes of surface states $(\gamma j,\gamma' j')$-SS, $(\gamma j,\gamma' j)$-SS, and (p,γ)-SS in the SNLA are clearly classified. For each class of states we can specify the envelope function of eigenstates as well as the eigenenergy. Our results show that the case which was discussed by Mahan and Obermair[18] is only one special case, i.e., our (p,p')-BS. More importantly, the surface states in our theory seem to be very useful to understanding the behavior of the first and second top-surface excitons, even though they are presented by complicated equations and wave functions than those in theories within the NLA (Refs. 13–15) or results in the SNLA by Koster and Slater[17] and Mahan and Obermair.[18] It should be stressed again that in the SNLA, there are three classes of surface states, and that for two of the three, i.e., the $(\gamma j,\gamma' j')$-SS and $(\gamma j,\gamma' j)$-SS, we have to use integer values j,j' to distinguish the surface states. The energy scheme of five classes of states as presented in the paper is useful to consider the energy levels of surface states in comparison with the band energy. For example, from the scheme, we can immediately determine which class of states is the first and second surface states when there are four surface states belonging to two different classes of states.

Let us now discuss about the sign and magnitude of R and S. One can see that if the site shifts Δ_1 and Δ_2 have the same signs as in experimental observations[6] ($\Delta_1=-204$ cm^{-1} and $\Delta_2=-6$ cm^{-1}), then R and S have the same signs in general. The case in which R and S have opposite signs (with Δ_1 and Δ_2 have the same signs) leads to results of the radiative decay rates contrary to the observations presented in Sec. IV B. The numerical results given in Table I are also meaningful in the discussion about the value of $|R|$. It can be estimated that the value of $|R|$ is about ~5 cm^{-1}, because this is a case giving results which seem to be in agreement with experimental observations of Aaviksoo, Lippmaa, and Reinot[6] as well as of Nozue, Kawaharada, and Goto.[19]

At this point, there may arise a question about the role of S. As will be seen below, S plays an important role, even though its value is small. Let us consider $S=0$ in the case (p,γ)-SS. The following argument, however, is valid for all classes. If $S=0$, Eq. (49) becomes

$$\Delta_2\{A_5\cos[(N-1)(p+i\gamma)]+A_5'\cos[(N-1)(p-i\gamma)]\}$$
$$=\Delta_2\varphi_{N-1}=0 \tag{58}$$

and the difference equations (4)–(6) can be rewritten as

$$(\omega-E_0)\varphi_n=R(\varphi_{n+1}+\varphi_{n-1})(-N+1<n<N-1), \tag{59}$$

$$(\omega-E_N)\varphi_N=R\varphi_{N-1}, \tag{60}$$

$$(\omega-E_{N-1})\varphi_{N-1}=R(\varphi_N+\varphi_{N-2}), \tag{61}$$

[Eqs. (5) and (6) are equivalent to Eqs. (7) and (8)]. From Eq. (58) we can see that $\Delta_2=0\Rightarrow\varphi_{N-1}=0$. In this case, Eq. (60) $\Rightarrow\varphi_N=0$ and then Eq. (61) $\Rightarrow\varphi_{N-2}=0$, and then from Eq. (59) we have $\varphi_n=0$ for all n. Therefore, Δ_2 must be equal to zero if $S=0$. In other words, if $\Delta_2\neq0$, then $S\neq0$. Because of that, if we want to understand the delicate properties due to the difference between first and second surface layers, we should take into account the second-nearest-layer interaction, i.e., the SNLA. The reason for different superradiant decay rates of the first and second surface excitons has been understood physically as presented in the present paper. This is the first problem which can be explained within the framework of the SNLA. The theory can be further developed to other systems, for example, to the nonsymmetric system which have just been considered in the NLA.[20] Second, it is very interesting to understand what additional effects happen in the reflection and transmission of the systems, both symmetric and nonsymmetric systems in the framework of the SNLA. These problems will be addressed in the future.

ACKNOWLEDGMENTS

The authors wish to thank Dr. Y. Nozue, Professor Nguyen Ba An, Professor M. Kuwata-Gonokami, and Dr. Y. Segawa for valuable discussions. One of us (N.T.D) would like to express his deep gratitude to the Nishina Memorial Foundation for the fellowship. This work is supported by a Grant-in-Aid for Scientific Research on the Priority Area ‘‘Mutual and Quantum Control of Radiation and Electronic Systems’’ from the Ministry of Education, Science and Culture of Japan.

---

[1] V.M. Agranovich and O.A. Dubovski, Pis'ma Zh. Éksp. Teor. Fiz. **3**, 345 (1966) [JETP Lett. **3**, 223 (1966)].

[2] E. Hanamura, Phys. Rev. B **38**, 1228 (1988).

[3] L.C. Andreani, F. Tassone, and F. Bassani, Solid State Commun. **77**, 641 (1990).

[4] Y. Segawa, J. Kusano, Y. Aoyagi, S. Namba, D. K. Shuh, and R. S. Williams, in *Proceedings of the 19th International Conference on the Physics of Semiconductors, Warsaw, 1988*, edited by W. Zawadzki (IFPAS, Warsaw, 1989), p. 437.

[5] B. Deveau, F. Clerot, N. Roy, K. Satzke, B. Sermage, and D.S.

Katzer, Phys. Rev. Lett. **67**, 2355 (1991).

[6] Ya. Aaviksoo, Ya. Lippmaa, and T. Reinot, Opt. Specktrosk. **62**, 706 (1987); [Opt. Spectrosc. (USSR) **62**, 419 (1987)]; J. Lumin. **37**, 313 (1987).

[7] M. Kuwata-Gonokami (private communication).

[8] 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).

[9] H. Hoshi, K. Kohama, S. Fang, and Y. Maruyama, Appl. Phys. Lett. **62**, 3080 (1993).

[10] H. Akimichi, T. Inoshita, S. Hotta, H. Noge, and H. Sakaki, Appl. Phys. Lett **62**, 3158 (1993).

[11] T. Nonaka, Y. Mori, N. Nagai, Y. Nakagawa, M. Saeda, T. Takahagi, and A. Ishitami, Thin Solid Films **239**, 214 (1994).

[12] J. M. Tullet, Ph. Kottis, and M.R. Philpott, Adv. Chem. Phys. **54**, 303 (1983).

[13] V. I. Sugakov, Fiz. Tverd. Tela (Leningrad) **14**, 1711 (1973) [Sov. Phys. Solid State **14**, 1473 (1973)].

[14] V.I. Tovsenko, Chem. Phys. Lett. **68**, 483 (1979).

[15] H. Ueba and S. Ichimura, J. Phys. Soc. Jpn. **41**, 1975 (1976); **42**, 355 (1977); H. Ueba, *ibid.* **43**, 353 (1977).

[16] P.S. Stern and M. E. Green, J. Chem. Phys. **58**, 2507 (1973).

[17] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

[18] G. D. Mahan and G. Obermair, Phys. Rev. **183**, 182 (1969).

[19] Y. Nozue, M. Kawaharada, and T. Goto, J. Phys. Soc. Jpn. **56**, 2570 (1987).

[20] Nguyen Ba An and E. Hanamura, Mod. Phys. Lett. B **9**, 1609 (1995); J. Phys. Condens. Matter **8**, 2273 (1996).

[21] M.R. Philpott, Adv. Chem. Phys. **23**, 226 (1973); J. Chem. Phys. **58**, 588 (1973).

[22] V.M. Agranovich, Zh. Eksp. Teor. Fiz. **37**, 430 (1959) [Sov. Phys. JETP **37**, 307 (1960)].

[23] E. Hanamura, in *Optical Switching in Low-Dimensional Systems*, edited by H. Haug and L. Banyai (Plenum, New York, 1989), p. 203.