

SURFACE STATES IN THIN VERSUS THICK ORGANIC QUANTUM WELLS

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Received 6 September 1995

Surface states are studied in dependence on thickness of organic quantum wells within the nearest layer approximation. It is shown that there is a material-dependent critical thickness. Structures that have thickness thinner or thicker than the critical one, exhibit qualitatively different characteristics of surface states. Criteria for existence and sign rules for location of energy levels of surface states are established which are general and contain the results of the previous works as particular cases.

Interest in organic heterostructures appears to have greatly increased in recent years, especially since the successful growth of organic super-lattices.^{1,2} The optical properties of organic quantum wells (OQW's) are mainly due to Frenkel excitons and play a crucial role in realizing various types of future photonic devices. To properly understand the optical properties, one should first explore the electronic structures. In bounded systems like OQW's, the electronic structure may exhibit surface states (SS) which bring about interesting phenomena such as dead borders, excitation traps, etc. Naturally to imagine that characteristics of SS's in thin OQW's differ from those in thick ones. However, what is the critical thickness that separates between "thin" and "thick"? And, on what does this critical thickness depend? To answer the above-posed questions is an attempt of the present letter. Another attempt is to outline the main results regarding the number and the location of energy levels of possible SS's in dependence on the OQW's parameters.

Most of previous theoretical works dealt with hypothetical semi-infinite surface crystals obtained by cleavage between two adjacent crystalline planes of a perfect infinite crystal.³ This model, within the nearest neighbor approximation, leads to

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while the terms of the second kind are responsible for interactions between the excitons in different layers

$$H = \sum_{\mathbf{k}} \sum_{n=1}^N \left[E_n(k) B_{n\mathbf{k}}^+ B_{n\mathbf{k}} + \sum_{n'=1}^N 'R_{nn'}(k) B_{n'\mathbf{k}}^+ B_{n\mathbf{k}} \right], \quad (3)$$

where the prime excludes the term with $n' = n$, $B_{n\mathbf{k}}$, $B_{n\mathbf{k}}^+$ are operators of a 2D exciton with in-layer wave vector \mathbf{k} and energy $E_n(k)$ in layer n , and $R_{nn'}(k)$ the interaction between excitons in layers n and n' . Note that because of the image charge effect due to abrupt changes of the dielectric constants at the interfaces, exciton energies in different layers are, in general, different. This fact is essential for the appearance of surface states. In Refs. 9 and 10, a highly simplified model was adopted where $E_n(k) \equiv E(k)$, i.e. the n -dependence was neglected. Such a model misses distribution due to possible surface states.

The eigen-problem of (3) can of course be solved numerically. Numerical solutions, however, cannot make clear classification among the thus obtained eigenstates. As one might expect, due to the presence of the interfaces and to the inter-layer interaction, the eigenstates may be classified as propagating or localized states. To get an insight into the nature of the eigenstates, it is necessary to solve (3) analytically. This can be done by using some approximations. Making use of the fact that $R_{nn'}$ decrease quickly as a function of inter-layer separation,^{11,12} one can resort to the nearest layer approximation (NLA), second nearest layer approximation, third nearest layer approximation and so on. Let us limit our consideration to the NLA only. This approximation is valid for the structures in which $R \equiv R_{n,n\pm 1} \gg R_{n,n\pm m}$ with $m > 1$. Within the NLA, among the many parameters, there remain E_1, E, E_N (exciton energies in layers $n = 1, 1 < n < N, n = N$) and R (the interaction between two nearest layers). Using the eigenfunction by the Heitler–London–Heisenberg method⁶ and the Schrödinger equation for the OQW, we have obtained, for the eigenenergy \mathcal{E} and the extension coefficients g_n of the eigenfunction, the following set of difference equations:

$$(\mathcal{E} - E_1)g_1 = Rg_2, \quad (4)$$

$$(\mathcal{E} - E)g_n = R(g_{n-1} + g_{n+1}), \quad 1 < n < N, \quad (5)$$

$$(\mathcal{E} - E_N)g_N = Rg_{N-1}. \quad (6)$$

The general solution¹³ of (5) is a linear combination of the four functions $\exp[(\pm\kappa \pm ip)n]$ with κ and p real and normalized by the layer spacing c . It is easy to prove that the allowed values of κ and p are classified into two cases:

- Case (i): $\kappa = 0, p \neq 0$, which yield (α, β are some coefficients)

$$g_n = \alpha \cos(pn) + \beta \sin(pn) \quad \text{and} \quad \mathcal{E} = E + 2R \cos(p). \quad (7)$$

- Case (ii): $\kappa \neq 0, p = \pi l, l$ integers or zero, which yield (θ, ϑ are some coefficients)

$$g_n = (-1)^{nl} [\theta e^{\kappa n} + \vartheta e^{-\kappa n}] \quad \text{and} \quad \mathcal{E} = E + 2(-1)^l R \cosh(\kappa). \quad (8)$$

The states originating from Case (i) form an energy band and are called band states (BS's) or propagating states, whereas those originating from Case (ii) correspond to energy levels located outside the above-said band and are referred to as SS's or localized states. To find the number of BS's and SS's, we have to determine p and (κ, l) so that (7) and (8) satisfy the two special equations (4) and (6), too. As a result, we have obtained the following criteria

$$\begin{cases} t_M \leq |R| & : 0 \text{ SS (and } N \text{ BS's),} \\ t_m \leq |R| < t_M & : 1 \text{ SS (and } N - 1 \text{ BS's),} \\ |R| < t_m & : 2 \text{ SS's (and } N - 2 \text{ BS's),} \end{cases} \quad (9)$$

where $t_m = \frac{1}{2}|N|\Delta_1 + \Delta_N| - \sqrt{\delta}|/(N + 1)$, $t_M = \frac{1}{2}[N|\Delta_1 + \Delta_N| + \sqrt{\delta}|/(N + 1)$, $\delta = (N^2 - 1)(\Delta_1 - \Delta_N)^2 + (\Delta_1 + \Delta_N)^2$, $\Delta_1 = E - E_1$ and $\Delta_N = E - E_N$. The dominant contribution to E, E_1, E_N and R is the dipole-dipole interaction which can be evaluated by Fourier transformation^{11,12} with the effect of image charges taken into account.¹⁴ Suppose for simplicity that each molecule has an equal dipole-moment μ and the in-layer lattice basic vectors are \mathbf{a} and \mathbf{b} . Then, for \mathbf{u} parallel (\parallel) and perpendicular (\perp) to the layers, we have obtained

$$\Delta_1^\perp = 2\Delta_1^\parallel = \frac{2(\varepsilon_1 - \varepsilon)}{\varepsilon(\varepsilon_1 + \varepsilon)} W(\gamma_1), \quad (10)$$

$$\Delta_N^\perp = 2\Delta_N^\parallel = \frac{2(\varepsilon_1 - \varepsilon)}{\varepsilon(\varepsilon_2 + \varepsilon)} W(\gamma_2), \quad (11)$$

$$R^\perp = -2R^\parallel = -\frac{2}{\varepsilon} W(1), \quad (12)$$

where $\gamma_{1,2} = 2d_{1,2}/c$ with $d_1(d_2)$ the effective distance from layer 1(N) to the interface $W(x) = \frac{2\pi^2\mu^2}{ab} \sum_{\mathbf{g}} |\mathbf{g} + \mathbf{k}| \exp(-2\pi x c |\mathbf{g} + \mathbf{k}|)$, and \mathbf{g} the 2D reciprocal lattice vector.

In the simplified model^{9,10} ignoring the difference between dielectric constants of the OQW region and the surrounding media, i.e. when $\varepsilon_1 = \varepsilon_2 = \varepsilon$, it follows from (10) and (11) that $\Delta_1 = \Delta_N = 0$ yielding $t_m = t_M = 0$. Hence, in accord with (9), no SS's are possible. In this case we get the same eigenfunction as in Refs. 9 and 10, i.e. its extension coefficients $g_n = \sqrt{2/(N + 1)} \sin(n\pi/(N + 1))$, which are solely of propagation nature.

In another particular case studied in Ref. 6, when $\Delta_1 = \Delta_N = \Delta \neq 0$, we get instead of (2)

$$\begin{cases} \Delta^2 \leq R^2 & : 0 \text{ SS (and } N \text{ BS's),} \\ \left(\frac{N-1}{N+1}\right)^2 \Delta^2 \leq R^2 < \Delta^2 & : 1 \text{ SS (and } N - 1 \text{ BS's),} \\ R^2 < \left(\frac{N-1}{N+1}\right)^2 \Delta^2 & : 2 \text{ SS's (and } N - 2 \text{ BS's),} \end{cases} \quad (13)$$

Formally, our criteria (13) coincide with the criteria (2) for $N \gg 1$, i.e. for thick OQW's. For thin OQW's consisting of a few layers, the two sets of criteria strongly differ. Yet, the terminologies "thick" and "thin" have a relative sense only. We shall make this issue clearer now. Obviously, Criteria (2) and (13) are the same for $|\Delta/R| \leq 1$ when the OQW has no SS independent of its thickness. Also, for $|\Delta/R| \geq 2$, OQW's of any thickness possess 2 SS's because in this case the inequality $\Delta^2 > (N-1)^2 \Delta^2 / (N+1)^2 > R^2$ always hold. For such parameters one cannot distinguish between thin and thick samples arguing on the number of SS's. For $1 < |\Delta/R| < 2$, however, 1 or 2 SS's may arise depending on the OQW's thickness. Namely, there exists a critical thickness determined by $N = N_c = (|\Delta/R| + 1) / (|\Delta/R| - 1)$. We conventionally call the OQW thin (thick) if its number of layers $N < N_c$ ($N > N_c$). The characteristics of the eigenstates of thin and thick OQW's are different qualitatively. For thin OQW's i.e. $N < N_c$ (thick OQW's, i.e. $N > N_c$), there is 1 SS (there are 2 SS's). The possible number of SS's is thus changing from 1 to 2 when the OQW is going from "thin" to "thick". Figure 2 is a phase diagram representing the domains of 0, 1 and 2 SS's in dependence on the thickness N as well as on the ratio $|\Delta/R|$ (see figure caption). The possible existence of 1 SS is the merit of our criteria (13). Note that N_c can be very large when $|\Delta/R|$ is a little bit greater than 1. In this case Criteria (2) is invalid. For $|\Delta/R|$ close to but less than 2, Criteria (2) is valid for thick OQW ($N > N_c$) only. Our criteria (13) is applicable for arbitrary thickness giving 1 SS for $N < N_c$ (thin OQW's) and 2 SS's for $N > N_c$ (thick OQW's). The relative meaning of "thin" and "thick" can also be felt from the general geometry when $\Delta_1 \neq \Delta_N$. Figure 3 depicts $|R|/t_m$ and $|R|/t_M$ as functions of N for various values of $|R/\Delta_m|$ and $|R/\Delta_M|$ ($|\Delta_m| = \min\{|\Delta_1|, |\Delta_N|\}$, $|\Delta_M| = \max\{|\Delta_1|, |\Delta_N|\}$). From Fig. 3 for $|R/\Delta_m| = 0.8$ and $|R/\Delta_M| = 0.5$, we see $N_c \simeq 5$. Then, $|R| < t_m < t_M$ reveals 2 SS's for, say, $N = 7 > 5 \simeq N_c$ (thick OQW) in accord with (9). However, for $|R/\Delta_m| = 0.9$ and $|R/\Delta_M| = 0.6$, we have $N_c \simeq 9$. Then, for $N = 7 < 9 \simeq N_c$ (thin OQW), we have $t_m < |R| < t_M$ revealing 1 SS in accord with (9). Hence, OQW's of the same thickness $N = 7$ looks thick (thin) and have 2 (1) SS's for $|R/\Delta_m| = 0.8$ (0.9) and $|R/\Delta_M| = 0.5$ (0.6)!

Our general criteria (9) set the existence conditions for the number of SS's which depend on both the OQW's parameters (Δ_1, Δ_N, R) and its thickness ($\propto N$). In the remainder, we briefly summarize our results regarding location of energy levels of the possible SS's. This is determined by signs of Δ_1 and Δ_N . As seen from (10) and (11), the signs of Δ_1 and Δ_N are in turn governed by $\varepsilon, \varepsilon_1$ and ε_2 , and may be negative as well as positive. Our detailed analysis has established the following useful sign rules:

- When $\Delta_m \Delta_M < 0$ and there are 2 SS's, i.e. line 3 in (9) is met, one of the SS's lies above and the other below the energy band of the BS's.
- When $\Delta_m \Delta_M < 0$ and there is 1 SS, i.e. line 2 in (9) is met, the SS lies above (below) the energy band of the BS's, if $\Delta_M < 0$ ($\Delta_M > 0$).

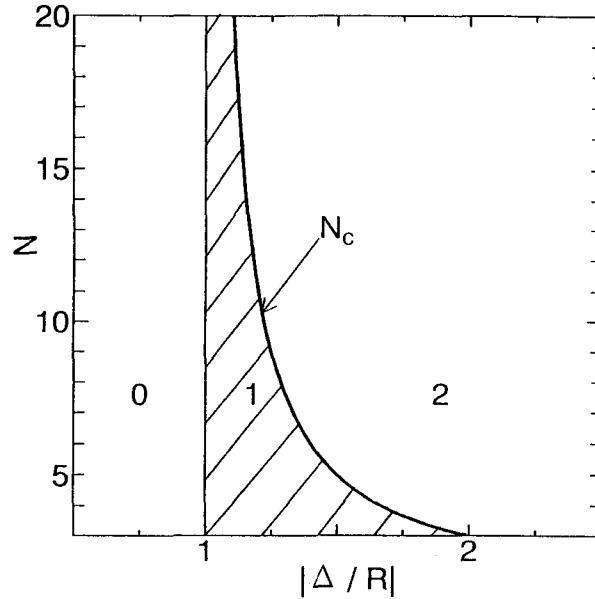


Fig. 2. Phase diagram versus N and $|\Delta/R|$. The boldface curve represents dependence of the critical number N_c of layers of the OQW on $|\Delta/R|$, i.e. $N_c = (|\Delta/R| + 1)/(|\Delta/R| - 1)$. The domain of existence of 1 SS is shaded and labelled 1. There are 2 (0) SS's in the domain labelled 2 (0).

- When $\Delta_m \Delta_M > 0$, no matter how many SS's arise, these SS's lie above (below) the energy band of the BS's if $\Delta_M < 0$ ($\Delta_M > 0$).
- As a particular situation, our treatment gives for the semi-infinite case the following results: there is 1 SS being located above (below) the energy band of the BS's, if $|\Delta| > |R|$ and $\Delta < 0$ ($\Delta > 0$). These conditions agree with (1).
- The sign of R plays no role in locating SS's but is of importance in describing the optical properties. As seen from (12), the sign of R is sensitive to polarization configurations.

It is worth noticing that the maximal number of possible SS's is 2 within the NLA. If we go beyond the NLA, say, to the second nearest layer approximation, the involved parameters will be $E_1, E_2, E, E_{N-1}, E_N, R$ and R' , where $E = E_n$ with $2 < n < N - 1$, $R \equiv R_{n,n\pm 1}$ and $R' \equiv R_{n,n\pm 2}$. Then, instead of 3 difference equations as in the NLA, there arise 5 equations which give at most 4 SS's. Therefore, discussion on the number of SS's is meaningful only on the basis of a certain approximation for the inter-layer coupling.

Measurements of picosecond decay rates of multi-layer anthracene samples have been done recently.^{15,16} In anthracene interfaced with air, R is much smaller than Δ and experiments might be compared with a theory¹⁷ that ignores the inter-layer interaction. Nevertheless, in other crystals, for example Kr, the ratio $|R/\Delta|$ seems as large as 0.64⁵ and, thus, the inter-layer interaction can by no means be neglected.

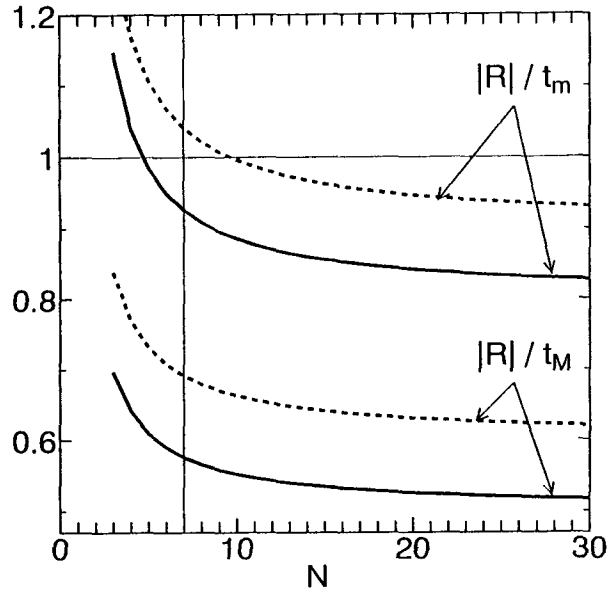


Fig. 3. $|R|/t_m$ and $|R|/t_M$ versus N in the case of $\Delta_m\Delta_M < 0$, for $|R/\Delta_m| = 0.8$, $|R/\Delta_M| = 0.5$ (solid curves) and $|R/\Delta_m| = 0.9$, $|R/\Delta_M| = 0.6$ (dashed curves). Intersections of the horizontal thin solid line with the curves $|R|/t_m$ determine the values of N_c . The vertical thin solid line at $N = 7$ is drawn to guide the eyes (see text).

In principle, as mentioned above, by sandwiching an OQW between different media the ratios $R/\Delta_{1,N}$ can be tailor-made by choosing appropriate ϵ_1 and ϵ_2 . Therefore, both the inter-layer interaction and interaction with radiation field should be taken into account on the same footing to explain the optical responses of OQW's. These deserve further efforts.¹⁸

Acknowledgments

We are grateful to Professor V. M. Agranovich for making Ref. 17 available to us prior to publication. Professors K. Miyano, M. Kuwata-Gonokami, K. Cho, H. Ishihara, H. Ueba, M. Yamanishi, T. Ishihara and M. Ueda for useful discussions. Part of this work was supported by JSPS and 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. One of us (N.B.A.) would like to thank the International Center for Theoretical Physics at Trieste and its Condensed Matter Group for hospitality.

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