

## Matching formalism for surface states and surface resonances

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A method for finding localized states and resonances at surfaces and at interfaces of periodic media, like solids or superlattices, has been formulated. The logarithmic derivatives of matched solutions in the case of localized states, and the local density of states in the case of resonances, are calculated using the concept of a *transfer matrix*. The method is applied to studying the electronic surface states in GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As superlattices and the image-induced resonances of the (111) surface of silver.

### I. INTRODUCTION

Fast developing experimental investigations of metal surface states, like crystal-derived states, image-induced localized states, or image resonances,<sup>1-6</sup> supply more and more accurate information about these states for nearly every metal surface. The two-dimensional surface states appear as a direct consequence of the breakdown of the three-dimensional translation symmetry in the  $z$  direction normal to the surface. Their existence is not therefore limited to the metal surfaces, but they can be looked for in any truncated periodic medium as, for example, superlattices.<sup>7-9</sup> The experimental interest is accompanied by an intensive effort in finding methods of theoretical description of the surface states. In contrast to simple approaches, such as multiple-scattering and phase-accumulation methods,<sup>10-13</sup> the surface-Green-function matching formalism,<sup>14</sup> based on the concept of the transfer matrix, has been recently put forward to study problems involving one or more interfaces.<sup>15</sup> The simple methods never go beyond the one-dimensional models, while the latter one is encumbered by some complexity, especially when trying to describe resonances.

The aim of this paper is to propose a matching formalism suitable for studying the localized states and resonances at surfaces and interfaces. The method exploits the concept of the transfer matrix<sup>16</sup> and is addressed to solving problems of matching states when the physical models of the matched media resolve themselves into systems of second-order differential equations. This happens, for example, when using the multiband pseudopotential models to describe crystallinity of the surfaces of solids,<sup>15</sup> or when using the envelope-function approximation for the multiband  $\mathbf{k}\cdot\mathbf{p}$  model to represent the band structure of semiconductor superlattices.<sup>17</sup>

In Sec. II the theoretical outline of the method is presented. In Sec. III the theory is applied to study surface states of GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As superlattices. In this study the terminated Kronig-Penney model is used and the results are compared with previous analytical calculations.<sup>9</sup> Next, the method is used to find the image-potential resonances of the Ag(111) surface. Concluding remarks are given in Sec. IV.

### II. THEORETICAL OUTLINE

Let us start with a system of  $N$  coupled ordinary linear homogeneous second-order differential equations:

$$\frac{d^2}{dz^2} \mathbf{f}(z) + \underline{\mathbf{B}}(z) \frac{d}{dz} \mathbf{f}(z) + \underline{\mathbf{C}}(z) \mathbf{f}(z) = 0. \quad (1)$$

The system can be transformed into a system of  $2N$  equations of the first order:

$$\frac{d}{dz} \mathbf{F}(z) + \underline{\mathbf{W}}(z) \mathbf{F}(z) = 0, \quad (2)$$

where

$$\mathbf{F}(z) = \begin{pmatrix} F_1(z) \\ F_2(z) \\ \vdots \\ F_{2N}(z) \end{pmatrix} = \begin{pmatrix} f_1(z) \\ \vdots \\ f_N(z) \\ f'_1(z) \\ \vdots \\ f'_N(z) \end{pmatrix},$$

$$\underline{\mathbf{W}}(z) = \begin{pmatrix} 0 & 1 \\ -\underline{\mathbf{B}} & -\underline{\mathbf{C}} \end{pmatrix},$$

and the prime means differentiation with respect to  $z$ . In general, the second derivative vector may be multiplied by a nonunit matrix  $\underline{\mathbf{A}}$ , but without losing much generality we can start with the form given by Eqs. (1). Equation (1), describing two different media separated by the geometrical plane at  $z=z_0$ , differs in the coefficient matrices  $\underline{\mathbf{B}}$  and  $\underline{\mathbf{C}}$ , and thus in the "potential"  $\underline{\mathbf{W}}$ . For each medium we define, following Mora, Pérez-Alvarez, and Sommers,<sup>16</sup> the transfer matrix which carries any solution of Eqs. (1) from a given point  $z_0$  (e.g.,  $z=0$ ) to a point  $z$  inside the desired medium:

$$\mathbf{F}(z) = \underline{\mathbf{M}}(z,0) \mathbf{F}(0), \text{ i.e., } \quad (3)$$

$$\begin{pmatrix} \mathbf{f}(z) \\ \mathbf{f}'(z) \end{pmatrix} = \begin{pmatrix} \underline{\mathbf{M}}_{AA} & \underline{\mathbf{M}}_{AD} \\ \underline{\mathbf{M}}_{DA} & \underline{\mathbf{M}}_{DD} \end{pmatrix} \begin{pmatrix} \mathbf{f}(0) \\ \mathbf{f}'(0) \end{pmatrix},$$

where  $\underline{M}_{ab}$  are  $N$ -dimensional blocks of the transfer matrix  $\underline{M}(z,0)$ .

In the present approach we are going to find the surface localized states by matching logarithmic derivatives (LD's) of the solutions of Eqs. (1) for both joined media, imposing proper boundary conditions (BC's) on the left and on the right of the surface in question. For the resonances, i.e., for the states which belong to the continuum energy region (to the band), the matching equations can have acceptable solutions for all energies. Therefore they are identified with the maxima of the local density of states.

Let us consider the problem of solutions and boundary conditions for two different kinds of media: (i) periodic, like solids or superlattices, and (ii) nonperiodic, like image barriers or outside step-well potentials. For the periodic media, according to Born-von Karman BC's the knowledge of  $\underline{W}$  limited to one period  $d$  is sufficient to determine an arbitrary solution of Eqs. (1). The transfer matrix which carries a solution by a single period is denoted  $\underline{M}(d)$ , i.e.,  $\underline{M}(d) \equiv \underline{M}(z+d, z)$ . Diagonalization of  $\underline{M}(d)$ , performed for all required energy values  $\mathcal{E}$ , allows us to solve the dispersion relation  $\mathcal{E}$  versus  $k$ .<sup>17</sup> The eigenvalues  $\lambda$  of  $\underline{M}$  can be expressed as  $e^{ikd}$  with  $k = q + i\kappa$  where  $q$  and  $\kappa$  are real. If  $\kappa = 0$  then the eigenvalues correspond to solutions  $f(z)$  which satisfy the Bloch periodicity condition

$$f(z+d) = e^{iqd} f(z). \quad (4)$$

Let us note that for a given energy  $\mathcal{E}$  more than one eigenvalue of  $\underline{M}$  may become equal to  $e^{iqd}$  for different values of  $q$ . This corresponds to several overlapping bands. The real values of  $k$  define thus the regions of allowed energies. Outside these regions there are no eigenvalues with  $\kappa = 0$ . The eigenvalues for which  $q = 0$  correspond to exponentially decaying solutions (purely imaginary  $k = i\kappa$ ):

$$f(z+d) = e^{-\kappa d} f(z). \quad (5)$$

For nonperiodic media, properties of the acceptable solution on the surface are determined by imposing appropriate BC's far from the surface, e.g., for  $z$  approaching infinity.

Let us consider now in detail the method of matching for localized surface states and for surface resonances.

#### A. Localized surface states

The localized surface states appear on the background of the forbidden energy regions (in the gaps) of a terminated periodic medium (i.e., joined with a nonperiodic one). For the nonperiodic side of the surface (let us say the left-hand one) we require that the solution corresponding to the localized state satisfy the condition

$$f(z) \xrightarrow{z \rightarrow -\infty} 0. \quad (6)$$

Let us define the logarithmic derivative  $\underline{L}^{(+)}$  of  $f$  at  $z = 0$  as

$$f'(0) = \underline{L}^{(+)} f(0). \quad (7)$$

From Eq. (3) we have

$$f(z) = (\underline{M}_{AA} + \underline{M}_{AD} \underline{L}^{(+)}) f(0), \quad (8)$$

and following condition (6) we may express  $\underline{L}^{(+)}$  as

$$\underline{L}^{(+)} = -\underline{M}_{AD}^{-1}(-) \underline{M}_{AA}(-), \quad (8a)$$

where  $\underline{M}_{AD}(-)$  and  $\underline{M}_{AA}(-)$  correspond to the transfer matrix calculated from  $z=0$  to  $-\infty$  (in practice to a sufficiently large value  $z_{-\infty}$ ). Let us note that the LD of  $f$  is exactly equivalent to the logarithmic derivative of the projection  $\underline{G} = \underline{G}(0,0)$  of the Green function  $\underline{G}(z,0)$  for this medium, defined in the surface-Green-function matching formalism (cf. Ref. 14), and expressed, similarly as in Eq. (8a), in terms of the transfer matrix. For the periodic medium (let us say the right-hand side of the surface) condition (6) does not define the LD uniquely at  $z=0$ . This is because  $f$  approaches zero nonmonotonically when  $z$  approaches infinity. As a consequence,  $\underline{L}^{(+)}$  is unstable with respect to changes of  $z_{\infty}$ . This instability is a direct consequence of the periodic structure of  $\underline{M}(z,0)$ . In order to find the logarithmic derivative of  $f(z)$  at  $z=0$ , we can take advantage of the fact that the required solution satisfies the condition (5), i.e.,

$$f(d) = \lambda f(0) \quad \text{for } \lambda = e^{-\kappa d}.$$

Thus from Eqs. (7), (3), and (5) we have

$$\underline{L} = -\underline{M}_{AD}^{-1}[\underline{M}_{AA}(d) - \lambda]. \quad (9)$$

Now, requiring continuity of  $f$  and  $f'$  through the surface or interface, we have

$$(\underline{L}^{(+)} - \underline{L}) f(0) = 0, \quad (10)$$

which implies that the localized states appear when

$$\det(\underline{L}^{(+)} - \underline{L}) = 0. \quad (11)$$

This can be used also to study interface-localized states of two periodic media using Eq. (9) to determine the LD on both sides of the interface plane. If for a given energy  $\mathcal{E}$  more than one eigenvalue  $\lambda$  of  $\underline{M}$  is real, we construct Eq. (11) for each  $\lambda$ . Equations (10) and (7) determine  $f(0)$  and  $f'(0)$ , respectively. Thus, with the given initial conditions, the wave function  $f(z)$  may be obtained by direct integration of Eqs. (1) from  $z=0$  to any point  $z$ . In the numerical code designed for practical applications, one can adopt the same integration procedure as the one used to determine  $\underline{M}$ .

We shall notice here that in the case of  $N=1$  the Green function  $\underline{G}(z,0)$  of the periodic medium, like  $f(z)$ , obeys condition (4) or (5). Thus Eq. (9) defines also uniquely the logarithmic derivative of the projection of the corresponding Green function. There is nothing peculiar in the fact that it depends on  $k$  (through  $\lambda$ ). This is always the case when we deal with one second-order differential equation, having one-to-one correspondence of  $\mathcal{E}$  and  $k$ .

#### B. Surface resonances

Let us now consider the case of the surface state energy  $\mathcal{E}$ , belonging to the continuum. The local density of

states (LDOS) on the surface separating two media at  $z=z_0$  is<sup>18</sup>

$$\sigma(z_0, \mathcal{E}) = \frac{1}{\pi} \text{Tr} \text{Im} \underline{G}(z_0, z_0; \mathcal{E}), \quad (12)$$

where  $\underline{G}(z, z'; \mathcal{E})$  is the surface (composite) Green function of Eqs. (1). According to the Green-function matching analysis,<sup>14,18</sup> the inversion of the surface projection  $\underline{G} = \underline{G}(z_0, z_0)$  of the Green function is related to the left- and right-hand side logarithmic derivatives  $\underline{L}_{\mathcal{G}}^{\ell}$  and  $\underline{L}_{\mathcal{G}}^r$  of the Green functions of two component media, respectively, as

$$\underline{G}^{-1} = \underline{L}_{\mathcal{G}}^{\ell} - \underline{L}_{\mathcal{G}}^r. \quad (13)$$

The main problem is now to find the LD's for both joined media. For the nonperiodic medium (the left one), the derivatives can be determined from the requirement that  $\mathcal{G}(z, z_0)$  remains regular when  $z \rightarrow -\infty$ . This is equivalent to our condition (6) for  $\mathbf{f}$ , and gives  $\underline{L}_{\mathcal{G}}^{\ell} = \underline{L}_{\mathcal{G}}^{(+)}$  [cf. Eqs. (8a)].

For the periodic medium we consider only the case when for a given energy  $\mathcal{E}$  only one complex and normalized  $\lambda$  appears. For example, this is always the case when  $N=1$ . As mentioned previously, the logarithmic derivative  $\underline{L}_{\mathcal{G}}^r$  is in such a case equivalent to the LD of  $\mathbf{f}$ , i.e.,

$$\underline{L}_{\mathcal{G}}^r = -\underline{M}_{AD}^{-1}(d)[\underline{M}_{AA}(d) - \lambda]. \quad (14)$$

Now, the inversion of  $\mathcal{G}$  defined by Eqs. (13), (14), and (6), allows us following Eqs. (12) to determine the LDOS  $\sigma$  on the surface. Let us note that even if  $\underline{W}$  and  $\underline{M}$  are real, the  $\mathcal{G}^{-1}$  is complex due to the complex  $\lambda = e^{iqd}$ , leading to nonzero density of states. This approach is applicable not only in the case of  $N=1$ . We can calculate  $\underline{L}_{\mathcal{G}}^r$  using Eqs. (14) for all the cases when for a given energy  $\mathcal{E}$  only one  $\lambda = e^{iqd}$  appears [i.e., only one acceptable solution of Eqs. (1) exist for this energy]. It happens, for instance, when there are no overlapping bands, which occurs often for  $\mathcal{E}$  near the edges of the allowed energy regions.

The problem appears when more than one complex and normalized  $\lambda$  simultaneously exist. This makes impossible the use of Eq. (14) to determine LD  $\underline{L}_{\mathcal{G}}^r$ . This problem deserves further investigation.

### III. APPLICATIONS

In this section the superlattice surface states (SSS's) of GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As, and the image-potential resonances (IR's) of Ag(111) are calculated as the illustration of the method presented. The results for SSS's are compared with the previous calculations based on the same model potential. The results for IR's are compared with experiment.

#### A. GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As superlattice surface states

A terminated Kronig-Penney (KP) model has been used to study the superlattice (SL) GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As surface states. In order to compare the present calculations with those by Stęślicka, Kucharczyk, and Glasser,<sup>9</sup> all the parameters of the model potential, i.e., the vacuum-well potential  $U$ , the conduction-band discon-

tinuity  $V_x$ , the band-gap difference  $\Delta E_{\Gamma x}$  at  $\Gamma$  minima of the composite layers, the effective masses  $m_1$ ,  $m_2$  and the thickness of the layers have been taken from their work:  $U=4.07$  eV,  $V_x=0.6\Delta E_{\Gamma x}$ ,  $m_1=0.067$ ,  $m_2=m_1+0.083x$ , GaAs and Al<sub>x</sub>Ga<sub>1-x</sub>As thickness are, respectively,  $a=60$  Å,  $b=15$  Å, and

$$\Delta E_{\Gamma x} = \begin{cases} 1.247x, & x < 0.45 \\ 1.247x + 1.147(x - 0.45)^2, & x > 0.45. \end{cases}$$

Our initial equation (1) is the Schrödinger equation with the  $U$  potential barrier outside of the superlattice and with the KP periodic potential representing the composite layers conduction-band edges. In this case the transfer matrices  $\underline{M}(-)$  and  $\underline{M}(d) = \underline{M}(a+b) = \underline{M}(a)\underline{M}(b)$  can be, for energy  $\mathcal{E} < U$ , put forward in the analytical forms

$$\underline{M}(-) = \frac{1}{2} \begin{bmatrix} (e^{\kappa\zeta} + e^{-\kappa\zeta}) & \frac{1}{\kappa}(e^{\kappa\zeta} - e^{-\kappa\zeta}) \\ \kappa(e^{\kappa\zeta} - e^{-\kappa\zeta}) & (e^{\kappa\zeta} + e^{-\kappa\zeta}) \end{bmatrix}, \quad (15)$$

where  $\zeta = z_{-\infty}$  and  $\kappa = [2(U - \mathcal{E})]^{1/2}$ , which gives  $\underline{L}^{(+)} = \kappa$  in the limit of  $\zeta \rightarrow -\infty$ . The matrix  $\underline{M}(a)$  reads

$$\underline{M}(a) = \begin{bmatrix} \cos(ka) & \frac{1}{k}\sin(ka) \\ -k\sin(ka) & \cos(ka) \end{bmatrix}, \quad (16)$$

where  $k = (2m_1\mathcal{E})^{1/2}$ . For  $\mathcal{E} > V_x$   $\underline{M}(b)$  takes the same form as  $\underline{M}(a)$  with  $k = [2m_2(\mathcal{E} - V_x)]^{1/2}$ , and for  $\mathcal{E} < V_x$   $\underline{M}(b)$  takes the same form as  $\underline{M}(-)$  with  $\zeta = b$  and  $\kappa = [2m_2(\mathcal{E} - V_x)]^{1/2}$ . The diagonalization of  $\underline{M}(d)$  allows us, according to Eqs. (4) and (5), to determine electronic structure, i.e., the minibands and minigaps of the conduction band of the compositional SL. Solving Eq. (11) for energies  $\mathcal{E}$  in the gaps, with the matrices  $\underline{M}(a)$  and  $\underline{M}(b)$  inserted into Eq. (9), we get the energies of the surface localized states. The results, for different composition  $x$ , are given in Fig. 1. They are the same as those

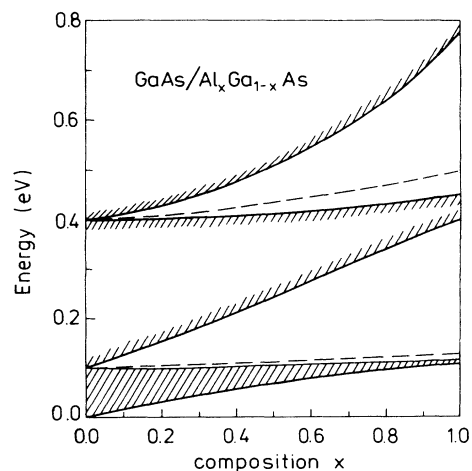


FIG. 1. Energy spectrum of GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As SL surface vs composition  $x$ . Dashed curves represent the energy of surface states, hatched areas represent the energy minibands.

by Stęślicka, Kucharczyk, and Glasser.<sup>9</sup> The existence of the surface resonances has also been checked using formula (12), but no peaks in  $\sigma$  versus  $\mathcal{E}$  have been noticed. This is in agreement with a recent observation<sup>19</sup> that resonance states do not appear in models with a step barrier terminating a semi-infinite crystal.

Also the calculated wave functions and probability densities of the surface states have exactly the same profiles as those presented by Stęślicka, Kucharczyk, and Glasser.<sup>9</sup> This is not shown here in order to avoid redundant repetition of the same results. It is important to note that applicability of the matching formalism presented here is not limited to simple one-band models, but can be easily applied within elaborated models represented by an arbitrary number of differential equations.

### B. Image-induced surface resonances of Ag(111)

Many experimental and theoretical papers on the image-potential induced states at metal surfaces have been recently published.<sup>1-6,10-13</sup> The majority of theoretical contributions is based on the phase-accumulation and multiple-scattering methods. A more sophisticated approach has recently been proposed by Jaskólski, Velasco, and García-Moliner.<sup>15</sup> In the same paper a brief review of the subject is given. But so far the main effort has been focused on studying image localized surface states occurring in the forbidden energy gaps. There is, however, experimental evidence<sup>1,3,4</sup> for the existence of the image surface resonances, e.g., image states situated on the continuum background of the conduction band. The main difficulty of theoretical description of surface resonances is due to their energetic degeneracy with the bulk band Bloch states.

The matching formalism presented in this paper may also be used to study image-induced resonances. The resonances are identified with the peaks of LDOS  $\sigma$  at the surface. We apply the formalism to describe the image resonances of Ag(111). We limit our consideration to a two-band pseudopotential model built on the reciprocal-lattice vectors  $\mathbf{g}$  responsible for opening the gap on the surface in question. The  $z$ -dependent bulk pseudopotential reads

$$V(z) = V_{000} + 2V_{111}\cos(g_z z), \quad (17)$$

where  $V_{111}$  is taken to be one half the gap at the  $\bar{\Gamma}$  point of the two-dimensional Brillouin zone (BZ) of the (111) surface. The surface image-barrier potential has been assumed as

$$V(z) = V_0 - \frac{1}{4(z - z_1)}. \quad (18)$$

The position  $z_i$  of the classical image plane is taken to have a value  $z_i = 2.0 \text{ \AA}$ , similar to the values used in previous calculations.<sup>15</sup> The vacuum level  $V_0$  we take equal to  $(\hbar^2/4m)(2\pi/a)^2$ , positioning it exactly in the middle of the gap at the (001) surface.<sup>1</sup> With these parameters the vacuum level falls about 1 eV above the conduction-band edge at  $\bar{\Gamma}$  of the (111) surface.

The local density of the surface states has been calcu-

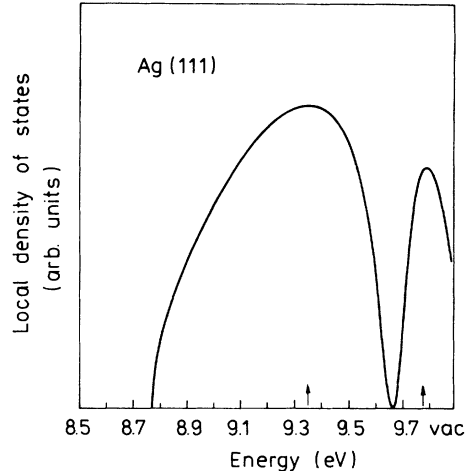


FIG. 2. Surface density of states  $\sigma$  in the conduction band below the vacuum level for Ag(111). Arrows indicate two peaks identified with  $n=1$  and  $n=2$  image-induced resonances.

lated using the recipe described in the theoretical outline. The transfer matrices  $\underline{M}(-)$  and  $\underline{M}(d)$  have been calculated integrating Eq. (2) in the canonical basis at  $z=0$ . The Adams-Moulton algorithm<sup>20</sup> has been used to perform the numerical integration. To diagonalize  $\underline{M}(d)$  the standard *EISPACK* (Ref. 21) subroutines have been used in both cases (IR and SSS). The results are presented in Fig. 2. The energy scale begins with zero of the bulk pseudopotential (17). The density of states vanishes for energies below the 8.77 eV band edge. Two peaks at energies just above the band edge represent  $n=1$  (9.35 eV) and  $n=2$  (9.78 eV) image resonances. Referring to the vacuum level (9.89 eV) their energies are 0.54 and 0.11 eV, respectively. The first one agrees quite well with that observed by Altmann (see Ref. 1) as 0.6 eV. The asymptotic form of the image potential is responsible for an infinite series of the Rydberg states converging to the vacuum level. Very seldom can more than two of them be obtained in either experimental or in theoretical investigations. We should mention here a very recent work by Radny.<sup>19</sup> The Green-function factorization theorem is applied there to a particular model, and used to investigate resonances at Al(001) and Al(111) surfaces. Similarly as in our approach the resonances are identified with the peaks of the LDOS.

## IV. CONCLUSIONS

A simple matching formalism to investigate electronic states of surfaces and interfaces of periodic media has been presented. To illustrate its usefulness the method has been applied to calculate semiconductor superlattice localized surface states and image resonances of metal. In the forbidden energy regions the logarithmic derivatives of the solutions of differential equations (1), for both sides of the interface, have to be matched in order to find the localized state. In the allowed regions (the bands), the expected resonances are identified as peaks of LDOS, again determined with the help of the logarithmic deriva-

tives. Imposing suitable BC's on the solutions at the left and at the right-hand side of the surface, all the required objects are expressed in terms of the transfer matrices. For nonperiodic media, the condition that the solution vanishes far from the surface suffices to determine the logarithmic derivative at the surface, as in the Green-function matching formalism. For periodic media the central role is played here by eigenvalues of the transfer matrix  $\underline{M}$  determined over one period. Establishing relations between the eigenvalues of  $\underline{M}$  ( $\underline{M}$  transfers solutions through one period) and the Bloch condition (4) for the allowed energies or the exponential decay condition (5) for forbidden energies is the most essential advantage of this formalism. This serves to find the logarithmic derivatives which are to be matched or used to determine  $\sigma$  at the surface. This way of finding LD's eliminates the difficulties which occur when LD's are determined from

the requirement of vanishing of the solution at infinity inside the periodic bulk.

Although the theory has been applied to simple models, based on a single second-order differential equation, it is clear that the same approach may also be used in more complex cases. Detailed investigations are in progress.

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