A note on a wavefunction formulation of the Korringa–Kohn–Rostoker method for calculating the electronic structure of layered systems

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Abstract. With the formal similarity between three-dimensional layered systems and one-dimensional chains of potential wells in mind, we discuss the wavefunction formulation of the Korringa–Kohn–Rostoker (KKR) formalism in one spatial dimension. We show that screening allows the construction of wavefunctions for such interesting non-periodic chains as two semi-infinite bulks separated by a spacer segment. We also discover a powerful analogue of the Friedel sum usually associated with scattering of electrons by point defects.

1. Introduction

Recently, multiple-scattering methods for solving the self-consistent Schrödinger equation for electrons in periodic solids, such as the Korringa–Kohn–Rostoker (KKR) [9, 10] and linear muffin-tin orbital (LMTO) methods, have undergone a remarkable revolution. In short, the problem has been reformulated in terms of scattering from a reference system [11], which is not free space, and the freedom of choice offered by the arbitrariness of the reference system has been exploited to make the structure constants of the theory short ranged [1, 2, 15, 18]. One of the more spectacular consequences of this screening transformation is that it rendered the calculation of the electronic structure of semi-infinite systems, such as a crystal with a surface, tractable [15]. In this paper we wish to comment on the way in which these novel calculations proceed.

Usually, for infinite bulk systems, the KKR band theory is presented as a Green's function method whilst the LMTO approach is developed in the language of wavefunctions. Although the two approaches are strictly equivalent in numerical implementations, they offer different sets of advantages and disadvantages [16]. Clearly, this is bound to be the case for problems involving surfaces and interfaces as well, and thus, both need to be developed. Since the applications of the screened KKR and LMTO methods to such problems have been exclusively Green's function calculations, we thought it worthwhile to explore the salient features of the corresponding wavefunction formulation. In this paper we report our findings in the context of a very simple, but nevertheless very suggestive, model and illustrate them with explicit calculations.

In sections 2 and 3.1 we set out the formalism and define the problem. The rest of section 3 is taken up with a formal solution for the wavefunction. It appears here to be helpful to introduce a transfer matrix and phase shifts in a way adapted to the present situation. This section concludes with explicit calculations of generalized phase shifts which can also be

interpreted as the integrated density of states as will be shown in section 4. Here, phase shifts are defined directly via the asymptotic behaviour of wavefunctions. They are presumably the same phase shifts as those discussed in reference [17] where they are defined in terms of the characteristic eigenvalue-resolved integrated density of states $N_\lambda(\epsilon)$. In this reference the connection of phase shifts to quantum well states is shown and a method to calculate them in a Green's function formalism is developed. In addition to providing a new way of computing them, our wavefunction approach sheds new light on the whole concept of phase shift in the present context.

Section 4 deals with the calculation of expectation values and we derive an analogue of Friedel's formula [8] for the integrated density of states, equation (48) below, induced by a slab inserted between two semi-infinite pieces of the host. This section is closed with a presentation of numerical results for charge oscillations in an inhomogeneous chain of potential wells analogous to a tri-layer system in three dimensions. Our comments are summarized in section 5.

2. Spherical harmonics for one-dimensional problems

In order to keep the present paper as self-contained as possible, we repeat here the basic notions necessary in the formulation of the KKR formalism in one dimension [4, 5, 12, 13].

Let R_i be a point on the real axis. We can then describe every point x by giving its distance $r_i = |x - R_i|$ and the direction $\hat{x}_i = (x - R_i)/r_i$ with respect to R_i. Evidently $\hat{x}_i$ is the one-dimensional analogue of the angles Θ and ϕ in three-dimensional polar coordinates. With this convention we can write for every x

$$x = r_i \hat{x}_i + R_i. \tag{1}$$

In general, any function $f(x)$ can be written as a sum of an even and an odd contribution with respect to R_i:

$$f(x) = f_0(r_i)Y_0(\hat{x}_i) + f_1(r_i)Y_1(\hat{x}_i) \tag{2}$$

with

$$f_0(r_i) = \frac{1}{\sqrt{2}} \left(f(R_i + r_i) + f(R_i - r_i) \right)$$
$$f_1(r_i) = \frac{1}{\sqrt{2}} \left(f(R_i + r_i) - f(R_i - r_i) \right) \tag{3}$$

and

$$Y_0(\hat{x}_i) = \frac{1}{\sqrt{2}} \qquad Y_1(\hat{x}_i) = \frac{\hat{x}_i}{\sqrt{2}}. \tag{4}$$

This expansion is unique and can be viewed as the analogue of the spherical harmonics expansion in three dimensions.

We will use the following complete set of solutions to the free-particle Schrödinger equation:

$$j_0(\sqrt{E}r) = \cos(\sqrt{E}r) \qquad j_1(\sqrt{E}r) = \sin(\sqrt{E}r) \tag{5}$$

and

$$h_0(\sqrt{E}r) = e^{i\sqrt{E}r} \qquad h_1(\sqrt{E}r) = -ie^{i\sqrt{E}r}. \tag{6}$$

Normally, all of these functions will appear in products containing the corresponding one-dimensional spherical harmonic Y_l. Therefore, we will use the notation

$$j_L(E, x_i) = j_L(\sqrt{E}r_i)Y_L(\hat{x}_i) \qquad L = 0, 1 \tag{7}$$

and similarly for n and h when appropriate.

3. Solving the screened KKR equation for the wavefunction

3.1. The screened KKR equation

The multiple-scattering KKR equations for the wavefunction amplitudes b_L^i read as follows [5, 12]:

$$\sum_{i',L'} \left((t_L^i(E))^{-1} \delta_{ii'} \delta_{LL'} - g_{LL'}^{ii'}(E) \right) b_{L'}^{i'} = 0 \tag{8}$$

where t_L^i is the L-component of the scattering matrix of the potential centred at site i. Remember that L in the one-dimensional case considered here can take only the values 0 and 1 corresponding to the two different point symmetries that a function can have in one-dimensional space, whereas in the three-dimensional case $L = (l, m)$ runs over all the infinitely many angular momentum (l) and magnetic (m) quantum numbers. $g_{LL'}^{ii'}$ are the structure constants which in the one-dimensional case have a very simple analytic form [4, 5, 12]. The coefficients $b_{L'}^{i'}$ determined by the KKR equation are related to the wavefunction in the interstitial region near site i by

$$\psi(E, x) = \sum_L b_L^i \left(i\sqrt{E} (t_L^i(E))^{-1} j_L(E, x_i) + h_L(E, x_i) \right). \tag{9}$$

After applying a screening transformation (see appendix A) the KKR equation takes on the form

$$\sum_{i',L'} \left(\tau_{LL'}^{r,ii'}(E) + \delta_{ii'} \delta_{LL'} (\delta m_L^i(E))^{-1} \right) \beta_{i'}^{L'} = 0 \tag{10}$$

with

$$\delta m_L^i = (t_L^i)^{-1} - (t_L^r)^{-1}. \tag{11}$$

t^r is the single site t-matrix of a suitably chosen reference system assumed to be site independent and τ^r is the scattering path matrix of the reference system determined by

$$\tau^r = ((t^r)^{-1} - g)^{-1}. \tag{12}$$

Evidently, in this screened representation τ^r plays the role of the structure constants $g^{ii'} LL'$ in the unscreened representation. The original wavefunction coefficients b_L^i are connected to the amplitude β_i^L, in the screening representation, by

$$b_L^i = \delta m_L^i \beta_i^L. \tag{13}$$

In our previous paper [12] we derived an analytic expression for $\tau_{LL'}^{r,ii'}$ and discussed its exponential decay with increasing site distance $|i - i'|$. According to what was said there, we may set the matrix elements of τ^r to zero whenever the site indices j and i fulfil $|j - i| > n$ for some suitably chosen n, where in our numerical calculations $n = 3$ turned out to be sufficient. This way, the 'screened' KKR matrix elements are given by

$$M_{LL'}^{ii'} = \tau_{LL'}^{r,ii'} + \delta_{ii'} \delta_{LL'} (\delta m_L^i)^{-1} \tag{14}$$

and the matrix $M_{LL'}^{ii'}$ is seen to be a banded matrix. That the coupling of one site is restricted to just neighbouring sites (up to the nth-nearest neighbours) allows us to split the complete chain into different regions for each of which the KKR equation can be solved independently. The effect of the neighbouring regions has then to be incorporated in certain boundary conditions, as will be seen below in subsection 3.4.

We restrict ourselves to systems where the chain of potentials can be divided into three regions in the following way (see figure 1): regions I and III contain all sites for which $i < -i_1$
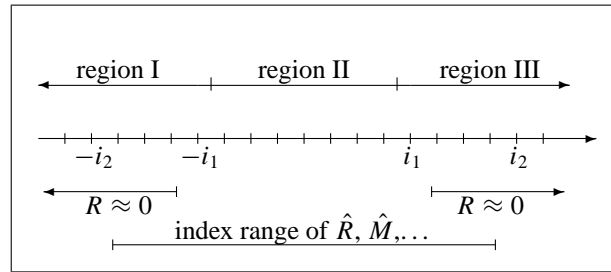
Figure 1. Here the index range is illustrated for some quantities. n which determines the width of the banded matrix is assumed to be 3. In region II the single-site potentials are arbitrary whereas the single-site potentials in regions I and II are all identical to each other.

or $i > i_1$ respectively. In these two regions all the muffin-tin potentials are the same, say $V_i = V_\infty$. Region II is finite and contains all sites in between site $-i_1$ and site i_1. In this region the muffin-tin potentials can be different from each other.

It will turn out that in this situation the problem of solving equation (10) is formally very close to the problem of constructing scattering states for a single finite-ranged potential well. In particular, we can introduce phase shifts and, exactly as in ordinary scattering theory, these phase shifts can be related to the integrated density of states. The role analogous to that of free space in scattering theory is taken here by the periodic chain of potentials consisting of potentials $V_i = V_\infty$ throughout the whole chain, referred to in the following as the homogeneous chain—or, alternatively, we shall refer to the homogeneous chain as the host and the central inhomogeneity as the defect.

3.2. The homogeneous chain

From Floquet's theorem [6, 7] it is clear that for every energy there exists a solution β_j^L for the homogeneous chain of the form $\beta_j^0 = v_0 e^{ikj}$, $\beta_j^1 = iv_1 e^{ikj}$, where $k = k(E)$ is real inside the band and complex with non-vanishing imaginary part inside band gaps. The coefficients v_0 and v_1 can be determined from the lattice Fourier-transformed unscreened KKR equation, which is given explicitly in reference [12], and the screening transformation equation (13). To simplify the algebra in what follows we shall regard the coefficients v_0 and iv_1 as well as β_j^0 and β_j^1 as components of two-component vectors. For energies inside a band (which is the case to which we restrict ourselves in this paper), v_0 and v_1 can be chosen to be real and for every solution of the form

$$\beta_j^{\mathrm{hom},1} = \begin{pmatrix} v_0 \\ iv_1 \end{pmatrix} e^{ikj} \tag{15}$$

there is another, independent solution at the same energy given by

$$\beta_j^{\mathrm{hom},2} = \begin{pmatrix} v_0 \\ -iv_1 \end{pmatrix} e^{-ikj}. \tag{16}$$

As the Schrödinger equation is a second-order linear differential equation, these two solutions form a complete set. A more convenient symmetry-adapted choice is given by

$$J_j^0 = \frac{1}{\sqrt{2}} (\beta_j^{\mathrm{hom},1} + \beta_j^{\mathrm{hom},2}) = \sqrt{2} \begin{pmatrix} v_0 \cos kj \\ -v_1 \sin kj \end{pmatrix} \tag{17}$$

and

$$J_j^1 = \frac{1}{\sqrt{2}i}(\beta_j^{\mathrm{hom},1} - \beta_j^{\mathrm{hom},2}) = \sqrt{2}\begin{pmatrix} v_0 \sin kj \\ v_1 \cos kj \end{pmatrix}. \tag{18}$$

J^0 is unchanged under reflection at site $j = 0$ ($j \to -j$; $v_L \to (-1)^L v_L$) whereas J^1 changes sign under reflection. Clearly this is of special advantage when the potential chain is symmetric under this transformation. When we demand β to be a solution to the KKR equation for the homogeneous chain at every site, i.e. for every i in equation (10), β can be written as a superposition of the two special solutions just given. However, when we insist on the KKR equation only for sites in regions I and III and do not care about sites in region II, there is no reason any more for β to be the same linear combination of our special solutions on the left as on the right of region II. The components β_j for $j > 0$ are completely independent of the components β_j for $j < 0$. Therefore we can construct two further independent solutions which we will call the irregular solutions in the following way:

$$\begin{aligned} N_j^0 &= \begin{cases} -J_j^1 & \text{for } j < 0 \\ J_j^1 & \text{for } j > 0 \end{cases} \\ N_j^1 &= \begin{cases} J_j^0 & \text{for } j < 0 \\ -J_j^0 & \text{for } j > 0 \end{cases} \end{aligned} \tag{19}$$

respecting again the symmetry in the sense that N^0 is symmetric and N^1 is antisymmetric under reflections at site $j = 0$. The values for $j = 0$ can be set to 0.

3.3. Asymptotics and phase shifts

Our intention is to use the set of four vectors defined above to describe the behaviour of the solutions to the KKR equation for the inhomogeneous chain asymptotically far away from region II. Clearly, in the vicinity of the inhomogeneity, it will not be possible to write the solution as a superposition of the homogeneous solutions J_L and N_L; thus we need an extra term to account for this pre-asymptotic behaviour. That is, we search for solutions to equation (10) of the form

$$\beta_j = \sum_{L=0}^{1} A_L J_j^L + \sum_{L=0}^{1} B_L N_j^L + C_j \tag{20}$$

where the correction C_j falls off exponentially outside the central segment containing the inhomogeneity. Note that L here refers to the symmetry under reflection of the *whole* chain. This way, the asymptotic behaviour of β is parametrized by the four real coefficients A_L, B_L and the pre-asymptotic corrections are given by C.

To show that a decomposition of the form of equation (20) is in fact possible, we will now consider an arbitrary solution of the screened KKR equation, equation (10), and will show that the physically relevant solutions can be written in the form given in equation (20). Equation (10) is a homogeneous linear equation with a banded matrix M given in equation (14) with only the $2n + 1$ central elements in every row being non-zero. This implies that $2n$ elements of β_j, say $(\beta_{j_1}, \beta_{j_1+1}, \ldots, \beta_{j_1+2n-1}) = x_{j_1}$ may be chosen arbitrarily. Equation (10) then implies that the elements $(\beta_{j_1+1}, \beta_{j_1+2}, \ldots, \beta_{j_1+2n}) = x_{j_1+1}$ can be obtained by a linear transformation from the chosen $2n$ elements x_{j_1}. And so can x_{j_1+2} be obtained from x_{j_1+1}, and so on. When all the indices involved are in region III, the matrix describing the step from x_j to x_{j+1} is always the same, independent of j, and so the mth power of this matrix determines the elements x_{j_1+m}. Now x_{j_1} can be decomposed into contributions which correspond to eigenvalues of

this matrix with modulus one, smaller than one, or bigger than one. The contributions of the first kind correspond to eigenmodes of the homogeneous system and therefore generate the homogeneous solutions properly described by the asymptotic part in equation (20). If the contribution corresponds to eigenvalues with modulus smaller than one its influence falls off exponentially and only the contribution corresponding to eigenvalues with modulus bigger than one are not within the realm of the *ansatz* equation (20). But these contributions lead to exponentially growing amplitudes and therefore are unphysical. In fact it will turn out that the coefficients A_L and B_L will be determined by demanding these exponentially growing contributions not to appear. The situation is somewhat similar to a single (three-dimensional) potential well at negative energies. When the Schrödinger equation for this case is integrated outwards starting from inside the potential well, there will also be contributions, in general, which blow up exponentially outside the potential well. The eigenenergies are determined as those energies at which these contributions do not appear. On the other hand, there are important differences between this case and the situation discussed here which are due to the fact that we are dealing here with discrete quantities and not with continuous functions. In our case, for example, the exponentially growing contributions appear also for energies at which the reference system has periodic solutions in contrast to the potential well where the asymptotic solutions are either oscillating or show exponential behaviour depending on the energy.

For further reference we rewrite equation (20) in the form

$$\boldsymbol{\beta}_j = \frac{1}{2}(A_0 + B_1)(\boldsymbol{J}_j^0 - \boldsymbol{N}_j^1) + \frac{1}{2}(A_1 - B_0)(\boldsymbol{J}_j^1 + \boldsymbol{N}_j^0)$$
$$+ \frac{1}{2}(A_0 - B_1)(\boldsymbol{J}_j^0 + \boldsymbol{N}_j^1) + \frac{1}{2}(A_1 + B_0)(\boldsymbol{J}_j^1 - \boldsymbol{N}_j^0) + \boldsymbol{C}_j. \tag{21}$$

Here, the terms are arranged such that the first two terms on the r. h. s. vanish whenever $j < 0$ and the third and fourth term vanish if $j > 0$. In the trivial homogeneous case, where all the single-site potentials in the whole chain are the same, the solutions are clearly given by the two regular solutions $\boldsymbol{J}^L$, so in this case $B_L = 0$ and $\boldsymbol{C} = \boldsymbol{0}$ whereas A_L can be chosen arbitrarily. In the general case (i.e. arbitrary potentials in the intermediate region), we expect the asymptotic behaviour of the solutions $\boldsymbol{\beta}$ to be described by a two-dimensional subspace of the space spanned by the four vectors $\boldsymbol{J}_j^L$ and $\boldsymbol{N}_j^L$. That is, we have to find two linear relations between the coefficients A_L and B_L. In scattering theory the analogue to this linear relationship is described by the t-matrix. Here it will turn out that this relation can be expressed by a transfer matrix connecting the asymptotic behaviour to the left to the asymptotic behaviour to the right. In the case where the potential chain is symmetric with respect to site 0, the solutions can be chosen to be symmetric or antisymmetric, meaning that there is one relation between A_0 and B_0 and another one between A_1 and B_1 but coefficients with different L are unrelated. So we can write

$$B_L = -\tan\delta_L A_L \tag{22}$$

with phase shifts δ_L. The definition is such that the symmetric solution is asymptotically proportional to

$$\boldsymbol{\beta}_j = \sqrt{2}\begin{pmatrix} v_0\cos(k|j| + \delta_0) \\ -\operatorname{sgn} j\, v_1\sin(k|j| + \delta_0) \end{pmatrix} \tag{23}$$

and the antisymmetric solution is asymptotically proportional to

$$\boldsymbol{\beta}_j = \sqrt{2}\begin{pmatrix} \operatorname{sgn} j\, v_0\sin(k|j| + \delta_1) \\ v_1\cos(k|j| + \delta_1) \end{pmatrix} \tag{24}$$

as can be verified by using equation (22) in the asymptotic part of β as given in equation (20). Thus the term 'phase shift' is justified. We will see later that phase shifts can be introduced also for the non-symmetric potential chain. Phase shifts for one-dimensional scattering problems have already been introduced by Sugiyama [14]. But in Sugiyama's paper the phase shifts are defined with respect to a constant background potential (jellium) whereas our reference system is the homogeneous potential chain.

3.4. Calculation of the pre-asymptotic part

Before considering the question of how to determine the relations between the various coefficients A_L and B_L, i.e. the phase shifts or the transfer matrix, let us assume that we know the answer and turn to the determination of the pre-asymptotic correction C for a given set of A_L and B_L. To this end we first show that for β of the form of equation (20) the KKR equation actually reduces to a finite-dimensional matrix equation. The vector components $(MJ^L)_j$ and $(MN^L)_j$ are zero for $|j| \geqslant i_1 + n$ because J^L and N^L are solutions to the KKR equation for that range of site indices. (Remember that for these sites the single-site potentials are assumed to be all the same and that the KKR matrix couples one site only to neighbouring sites up to the nth-nearest neighbours.) Furthermore, C_j is supposed to be approximately zero for sufficiently large absolute values of the site index j, say $|j| \geqslant i_2 - n$. This ensures that $(MC)_j$ is zero whenever $|j| \geqslant i_2$, where $i_2 - n \geqslant i_1$ is assumed for a suitable choice of i_2 (cf. figure 1). Therefore, when only solutions of the form of equation (20) are considered, the KKR equation reads

$$\hat{M}\hat{C} = -\sum_{L=0}^{1} A_L \widehat{MJ^L} - \sum_{L=0}^{1} B_L \widehat{MN^L} \tag{25}$$

where the hat denotes restriction of the site indices to $|j| < i_2$. Note that $\widehat{MJ^L}$ is clearly *not* the same as $\hat{M}\hat{J}^L$. Equation (25) can be seen as the KKR equation for region II where the inhomogeneity, i.e. the right-hand side, is due to the prescribed asymptotic behaviour. As $\hat{M}$ is a finite-dimensional banded matrix the inversion can be done numerically, so $\hat{R}$ can be calculated from

$$\hat{C} = \sum_{L=0}^{1} A_L \hat{C}_L^{(J)} + \sum_{L=0}^{1} B_L \hat{C}_L^{(N)} \tag{26}$$

with

$$\hat{C}_L^{(J)} = -\hat{M}^{-1}\widehat{MJ^L} \qquad \hat{C}_L^{(N)} = -\hat{M}^{-1}\widehat{MN^L}. \tag{27}$$

C now is simply constructed from $\hat{C}$ by setting all the additional components to zero:

$$C_j = \begin{cases} \hat{C}_j & \text{for } |j| < i_2 \\ \mathbf{0} & \text{otherwise.} \end{cases} \tag{28}$$

3.5. Calculating the asymptotics

Recall that in deriving the finite-dimensional form of the KKR equation, equation (25), we assumed C_j to be zero for $|j| \geqslant i_2 - n$. By demanding this boundary condition to be fulfilled as well as possible, the relations between the coefficients A_L and B_L are determined. Numerically, this can be done by introducing the function

$$n(A_L, B_L) = \sum_{j=-i_2+1}^{-i_2+n} |\hat{C}_j|^2 + \sum_{j=i_2-n}^{i_2-1} |\hat{C}_j|^2 \tag{29}$$

with $\hat{C}$ taken as functions of A_L and B_L as given by equation (26). Minimizing it under the constraint $\sum_L (A_L^2 + B_L^2) =$ constant yields the eigenvalue equation

$$\mathcal{Y} \begin{pmatrix} A_0 \\ A_1 \\ B_0 \\ B_1 \end{pmatrix} = \lambda \begin{pmatrix} A_0 \\ A_1 \\ B_0 \\ B_1 \end{pmatrix} \tag{30}$$

with the 4×4 matrix

$$\mathcal{Y}_{ss'} = \sum_{j=-i_2+1}^{-i_2+n} \hat{C}_j^s \cdot \hat{C}_j^{s'} + \sum_{j=i_2-n}^{i_2-1} \hat{C}_j^s \cdot \hat{C}_j^{s'} \tag{31}$$

where the indices s and s' label the four combinations $(J, 0)$, $(J, 1)$, $(N, 0)$, $(N, 1)$ in this order. The eigenvalue λ is a Lagrange multiplier due to the constraint stated above. Two of the four eigenvectors correspond to minima of $n(A_L, B_L)$. Denoting them by superscripts (1) and (2), the general asymptotic behaviour consistent with the KKR equation is described by

$$\begin{pmatrix} A_0 \\ A_1 \\ B_0 \\ B_1 \end{pmatrix} = \sum_{r=1}^{2} \chi_r \begin{pmatrix} A_0^{(r)} \\ A_1^{(r)} \\ B_0^{(r)} \\ B_1^{(r)} \end{pmatrix} \tag{32}$$

with two arbitrary coefficients χ_r. Accordingly the general solution can be written as a super-position of the form

$$\beta = \sum_{r=1}^{2} \chi_r \left(\sum_L A_L^{(r)} (J^L + C_L^{(J)}) + \sum_L B_L^{(r)} (N^L + C_L^{(N)}) \right). \tag{33}$$

Equation (32) describes the possible asymptotic behaviour of the solutions and it is useful to recast it in a form explicitly displaying the transfer matrix $\mathcal{T}$. Equation (32) is equivalent to demanding that

$$\mathcal{T} \begin{pmatrix} A_0 + B_1 \\ A_1 - B_0 \end{pmatrix} = \begin{pmatrix} A_0 - B_1 \\ A_1 + B_0 \end{pmatrix} \tag{34}$$

which expresses the amplitudes describing the asymptotic behaviour to the right as a linear function of the amplitudes describing the asymptotic behaviour to the left. $\mathcal{T}$ in terms of the special solutions $A_L^{(r)}$, $B_L^{(r)}$ is given by

$$\mathcal{T} = \begin{pmatrix} A_0^{(1)} - B_1^{(1)} & A_0^{(2)} - B_1^{(2)} \\ A_1^{(1)} + B_0^{(1)} & A_1^{(2)} + B_0^{(2)} \end{pmatrix} \begin{pmatrix} A_0^{(1)} + B_1^{(1)} & A_0^{(2)} + B_1^{(2)} \\ A_1^{(1)} - B_0^{(1)} & A_1^{(2)} - B_0^{(2)} \end{pmatrix}^{-1}. \tag{35}$$

It may be helpful to note that we have arrived at the above relation by matching the part of the solution inside the potential range to the asymptotic part outside, similarly to the way in which in ordinary scattering theory the t-matrix is defined. Only the procedure of matching is different here.

Note that so far we have imposed no boundary conditions on β at infinity. In the next section we will remedy this omission.

3.6. Boundary conditions

With the method described in the previous section we find a two-dimensional space of solutions to the KKR equation (equation (10)) for every energy for which bulk solutions exist. In order to find the density of states and expectation values, we somehow have to apply further boundary

conditions which allow only for a discrete set of eigenenergies and well defined eigenvectors. Therefore, we will now investigate how periodic boundary conditions can be applied.

For j being a site in the asymptotic regime to the left, periodic boundary conditions imply

$$\sum_{L=0}^{1} (A_L \boldsymbol{J}_j^L + B_L \boldsymbol{N}_j^L) = \sum_{L=0}^{1} (A_L \boldsymbol{J}_{j+\mathcal{N}}^L + B_L \boldsymbol{N}_{j+\mathcal{N}}^L) \tag{36}$$

where $\mathcal{N}$ is the arbitrarily large periodicity length chosen. To get explicit expressions we choose the site index j such that $j < -i_2$ and $j + \mathcal{N} > i_2$. With this restriction for the site index, the asymptotic solutions $\boldsymbol{N}^L$ can be expressed in terms of $\boldsymbol{J}^L$ via equation (19). Furthermore, we have, from the explicit form for the $\boldsymbol{J}$ (equations (17) and (18)) and straightforward use of trigonometric identities,

$$\begin{aligned} \boldsymbol{J}_{j+\mathcal{N}}^0 &= \cos(k\mathcal{N})\boldsymbol{J}_j^0 - \sin(k\mathcal{N})\boldsymbol{J}_j^1 \\ \boldsymbol{J}_{j+\mathcal{N}}^1 &= \sin(k\mathcal{N})\boldsymbol{J}_j^0 + \cos(k\mathcal{N})\boldsymbol{J}_j^1. \end{aligned} \tag{37}$$

Thus equation (36) can be rewritten in a form only containing $\boldsymbol{J}_j^0$ and $\boldsymbol{J}_j^1$. Equating the corresponding coefficients yields after some algebra

$$\begin{aligned} \cos(k\mathcal{N})(A_0 + B_1) - \sin(k\mathcal{N})(A_1 - B_0) &= A_0 - B_1 \\ \sin(k\mathcal{N})(A_0 + B_1) + \cos(k\mathcal{N})(A_1 - B_0) &= A_1 + B_0. \end{aligned} \tag{38}$$

This equation has the same form as equation (34) with the transfer matrix $\mathcal{T}$ replaced by a rotation about the angle $k\mathcal{N}$. It has two important implications. Firstly, as the transfer matrix $\mathcal{T}$ is not, in general, unitary, equation (38) selects those vectors from the two-dimensional space described by equation (32) which have the same magnitude for the amplitude in the asymptotic regime to the right as to the left. That is,

$$(A_0 + B_1)^2 + (A_1 - B_0)^2 = (A_0 - B_1)^2 + (A_1 + B_0)^2. \tag{39}$$

Secondly, only those k-numbers for which $k\mathcal{N}$ is equal to the angle between the vectors $((A_0 + B_1), (A_1 - B_0))$ and $((A_0 - B_1), (A_1 + B_0))$ for those solutions just selected by the first implication are allowed by the periodic boundary conditions.

Equation (39) is equivalent to

$$A_0 B_1 - A_1 B_0 = 0 \tag{40}$$

which, due to equation (32), is a quadratic equation for χ_r, namely

$$\sum_{r,r'} \chi_r M_{rr'} \chi_{r'} = 0 \tag{41}$$

with

$$M_{rr'} = A_0^{(r)} B_1^{(r')} - A_1^{(r)} B_0^{(r')} + A_0^{(r')} B_1^{(r)} - A_1^{(r')} B_0^{(r)}. \tag{42}$$

The solutions can be written in terms of the eigenvectors $\vec{w}_1$ and $\vec{w}_2$ of the symmetric matrix M. Calling the respective eigenvalues ϵ_1 and ϵ_2, one easily checks that

$$\vec{\chi} = \sqrt{|\epsilon_2|}\vec{w}_1 \pm \sqrt{|\epsilon_1|}\vec{w}_2 \tag{43}$$

solves equation (41) if and only if $\epsilon_1 \epsilon_2 \leqslant 0$. It is important to note that equation (41) can be fulfilled not only for discrete values of k but also for whole intervals, in contrast to equation (38). Formally, this is due to the absence of the fast-oscillating trigonometric functions in equation (40) which are present in equation (38). Therefore by means of equation (41) and (32) the coefficients $A_{\nu L}$ and $B_{\nu L}$ are defined as smooth functions of k. The subscript ν labels the two solutions which result from the choice of sign in equation (43).

We now introduce the angle $2\delta_\nu = 2\delta_\nu(k)$ between the vectors $((A_{\nu0} + B_{\nu1}), (A_{\nu1} - B_{\nu0}))$ and $((A_{\nu1} - B_{\nu1}), (A_{\nu1} + B_{\nu0}))$:

$$\cos 2\delta_\nu = \frac{A_{\nu0}^2 + A_{\nu1}^2 - B_{\nu0}^2 - B_{\nu1}^2}{A_{\nu0}^2 + A_{\nu1}^2 + B_{\nu0}^2 + B_{\nu1}^2}$$

$$\sin 2\delta_\nu = -2\frac{A_{\nu0}B_{\nu0} + A_{\nu1}B_{\nu1}}{A_{\nu0}^2 + A_{\nu1}^2 + B_{\nu0}^2 + B_{\nu1}^2}. \tag{44}$$

The sign of the angle δ_ν and the prefactor 2 is chosen such that, in the case of a symmetric potential chain, δ_ν becomes the phase shift defined in equation (22) as will be shown below. With this definition, equation (38) implies

$$\delta_\nu(k) = -\frac{1}{2}k\mathcal{N} \pmod{\pi}. \tag{45}$$

This equation now determines the k-values k_ν allowed by the boundary conditions. The corresponding eigenstates are determined by the amplitudes $A_{\nu L}(k_\nu)$ and $B_{\nu L}(k\nu)$ and the eigenenergy is given by $E_\nu = E(k_\nu)$, where $E(k)$ is the dispersion relation of the homogeneous chain. The normalization of the eigenstates will be discussed in appendix B.

Herewith the construction of the solutions to the KKR equation is complete. In the next section we will discuss the calculation of expectation values. But before doing so let us once more specialize to the symmetric potential chain as an illustration. In the case of a symmetric potential chain we know that the solutions to the KKR equation can be chosen to be symmetric or antisymmetric. That is, $A_L^{(r)}$ and $B_L^{(r)}$ can be chosen to be of the form $A_L^{(r)} \propto \delta_{Lr}$ and $B_L^{(r)} \propto \delta_{Lr}$ with $r = 0$ labelling the symmetric solution and $r = 1$ labelling the antisymmetric solution. The diagonal elements of the matrix M defined in equation (42) are zero in this case and so $\chi = (1, 0)$ and $\chi = (0, 1)$ solve equation (41). That is, $A_0 = A_L^{(r)}$ and $B_L = B_L^{(r)}$, with $r = 0$ or $r = 1$, solve equation (40). This can be clearly seen directly and is expected from symmetry considerations. Using the symmetric solution ($A_1 = B_1 = 0$), equation (44) implies $\tan\delta = -B_0/A_0$ which is just the definition of the phase shift (equation (22)). Using the antisymmetric solution the same result is found. Equation (45), in the special case considered here, also follows directly by applying the periodic boundary conditions to equation (23).

As a typical example, in figure 2 the phase shifts $\delta_L(E)$ in units of π are shown for a chain of square-well potentials where the intermediate region (region II in figure 1) contains 18 sites with potential wells -0.2 Ryd deep. All the other wells are -0.5 Ryd deep. The Wigner–Seitz radius has been chosen to be 1 au and the lattice constant to be 2.2 au. For energies below -0.2 Ryd the curves drop significantly. This can be understood semiquantitatively in the following way: were the potential in the intermediate region the same as in the outer region, the integrated density per site would be $N_0(E)$, which for small energies behaves like $\sqrt{E - E_0}$ with $E_0 \approx -0.5$ Ryd. With the 18 potentials in the intermediate region only -0.2 Ryd deep, this space is not available any more for electrons with energy lower then -0.2 Ryd, so by this 'hand-waving' argument we would expect $(\delta_0(E) + \delta_1(E))/\pi \approx -18N_0(E)$, which in fact as we have checked is a fairly good approximation to the sum of the curves shown in figure 2 for energies in between -0.5 and -0.2 Ryd. Finally, it is interesting to note that, qualitatively, these curves look like phase shifts of a single repulsive potential well in one-dimensional space.

4. Calculation of expectation values

Some care is needed when calculating expectation values. When the properly normalized single-particle states are known, the ground-state expectation value of some one-particle
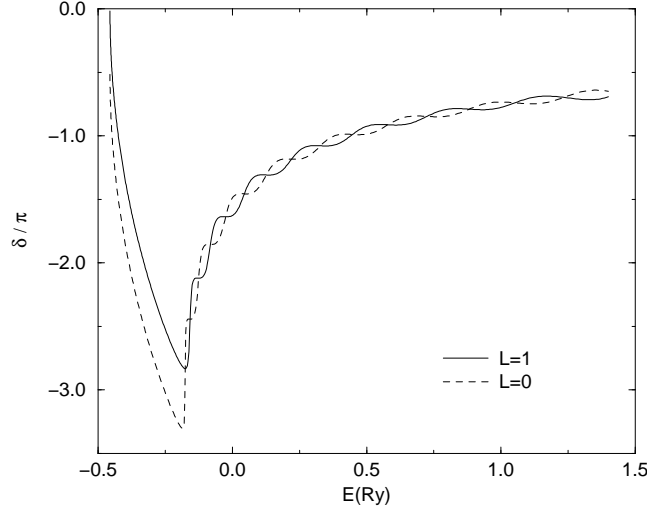
Figure 2. Here the phase shifts δ_L divided by π as a function of energy are shown. The parameters describing the underlying chain of square-well potentials are given in the text.

operator can be calculated as a sum over all the occupied states:

$$\langle \hat{O} \rangle = \sum_{i \text{ occ}} \tilde{o}_i \tag{46}$$

where $\tilde{o}_i$ is the expectation value of $\hat{O}$ in the single-particle state labelled by i. The aim of this section is to transform the sum into a k-space integral. This is easy for the homogeneous chain where the allowed k-values are given by

$$k = k_i^0 = \mathrm{i} \frac{2\pi}{\mathcal{N}}$$

and therefore are equidistantly distributed on the real axis. In the more general case where the potential chain is homogeneous only in the asymptotic regime we still can characterize the eigenstates by their asymptotic wavenumber k and a label ν which accounts for the two solutions of equation (41). We write the asymptotic wavenumber k as

$$k = k_i^\nu = \mathrm{i} \frac{2\pi}{\mathcal{N}} + \delta k_i^\nu = k_i^0 + \delta k_i^\nu.$$

Equation (45) implies that δk_i^ν can be identified up to a prefactor with the phase shift δ_i^ν associated with the state i: $\delta k_i^\nu = -2\delta_i^\nu / \mathcal{N}$. Thus, writing the one-particle expectation values as a function of k one can rewrite the sum as a k-space integral:

$$
\begin{aligned}
\langle \hat{O} \rangle &= \sum_\nu \sum_{i(k_i^0 - 2\delta_i^\nu / \mathcal{N} \leqslant k_F)} \tilde{o}^\nu \left(k_i - 2 \frac{\delta_i^\nu}{\mathcal{N}} \right) \\
&= \sum_\nu \frac{\mathcal{N}}{2\pi} \int_0^{k_F - \delta k_F^\nu} \mathrm{d}k \left\{ \tilde{o}^\nu(k) - 2 \frac{\mathrm{d}\tilde{o}^\nu}{\mathrm{d}k} \frac{\delta^\nu(k)}{\mathcal{N}} \right\} \\
&= \sum_\nu \left\{ \frac{\mathcal{N}}{2\pi} \int_0^{k_F} \mathrm{d}k \, \tilde{o}^\nu(k) + \frac{\delta^\nu(k_F)}{\pi} \tilde{o}^\nu(k_F) - \frac{1}{\pi} \int_0^{k_F} \mathrm{d}k \frac{\mathrm{d}\tilde{o}^\nu}{\mathrm{d}k} \delta^\nu(k) \right\} \\
&= \sum_\nu \left\{ \frac{\mathcal{N}}{2\pi} \int_0^{k_F} \mathrm{d}k \, \tilde{o}^\nu(k) \left(1 + \frac{2}{\mathcal{N}} \frac{\mathrm{d}\delta^\nu(k)}{\mathrm{d}k} \right) + \frac{\delta^\nu(0)}{\pi} \tilde{o}^\nu(0) \right\}. \tag{47}
\end{aligned}
$$

Thus the fact that the k-values which are allowed by the boundary conditions are not equidistant is reflected by a weight

$$1 + \frac{2}{\mathcal{N}} \frac{\mathrm{d}\delta^\nu(k)}{\mathrm{d}k}$$

in the k-space integral.

Clearly, the total number of states $N(E)$ below a given energy is an expectation value of special interest and is obtained by setting $\tilde{o} = 1$ in equation (47):

$$N(E) = \frac{\mathcal{N}}{\pi} k(E) + \frac{1}{\pi} \sum_\nu \int_0^{k(E)} \frac{\mathrm{d}\delta^\nu(k)}{\mathrm{d}k} \, \mathrm{d}k + \sum_\nu \frac{\delta^\nu(0)}{\pi} = N_0(E) + \sum_\nu \frac{\delta^\nu(E)}{\pi}. \tag{48}$$

This is the analogue to the relation known as the Friedel sum [8] which relates the phase shift at energy E to the integrated density of states $N(E)$. A completely different derivation of this result can be found in reference [17].

For other expectation values, the integral equation (47) has to be solved numerically. This task can be simplified by noting that the integration weight can be absorbed in the normalization of the wavefunction. As discussed in appendix B, the wavefunction

$$\tilde{\psi}^\nu(k, x) = \left(1 - \frac{1}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k}\right) \psi^\nu(k, x) \tag{49}$$

is normalized to 1 within the periodicity interval if $\psi^\nu(k, x)$ has asymptotically the same amplitude as the homogeneous solution. The point to note here is that the integrand

$$\tilde{o}^\nu(k) \left(1 - \frac{2}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k}\right) \approx \tilde{o}^\nu(k) \left(1 - \frac{1}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k}\right)^2$$

is the expectation value of $\hat{O}$ with the wavefunction $\psi^\nu(k, x)$ which is *not* normalized to 1 but normalized according to its asymptotic behaviour. Therefore we can write

$$\langle \hat{O} \rangle = \mathcal{N} \sum_\nu \int_0^{k_F} \mathrm{d}k \, o^\nu(k) \qquad \text{with } o^\nu(k) = \langle \psi^\nu | \hat{O} | \psi^\nu \rangle \tag{50}$$

which now is an ordinary k-space integral which contains no derivatives with respect to k.

As an example we have calculated the charge per site for the potential already described above with a Fermi energy of 1.4 Ryd. The result is shown in figure 3. The Friedel oscillations are clearly seen in both the intermediate and the outer region. As the Fermi energy is close to the upper edge of a band of the homogeneous chain, the oscillation wavelength in the outer regime is quite long. The Fermi energy is not so close to the edge of the homogeneous chain, consisting merely of 0.2 Ryd deep potentials, and therefore the wavelength of the charge oscillations in the intermediate regime is shorter. (For further discussion of Friedel oscillations in one-dimensional potential chains, see reference [12].)

5. Summary

We have shown how the solutions of the KKR equation for an inhomogeneous chain of potential wells in one spatial dimension can be constructed. For our method to work it was absolutely essential to have the idea of screening available, as only the bandedness of the KKR matrix allowed us to develop a formalism which, like in usual scattering theory, characterizes a solution, in the presence of a defect, completely by its asymptotic behaviour in the host. Indeed, we defined generalized phase shifts $\delta_L(E)$ which describe the scattering properties of an inhomogeneity in the potential. Interestingly, they are directly related to the integrated
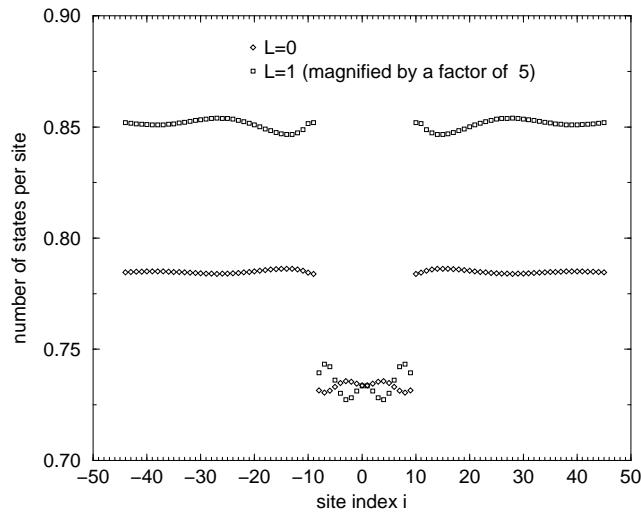
Figure 3. Here the charge per site and symmetry character ($L = 0$, $L = 1$) is shown. The Fermi energy (1.4 Ryd) was chosen to lie slightly below the upper band edge of the lowest-lying band.

density of states, in perfect analogy to Friedel's sum featured in the theory of scattering from point defects in three dimensions.

Evidently, in the case of an interface separating two regular arrays of potential wells, natural and powerful concepts for characterizing the electronic states of the perturbed system are the reflection and transmission coefficients [3, 17]. In the case of a deformed region completely embedded in a host, the generalized phase shifts that we have introduced above are similarly powerful tools. As we have demonstrated, our approach allows us to determine these phase shifts directly from the asymptotic behaviour of the wavefunctions. Thus it would be desirable to generalize the arguments of this paper to the three-dimensional case of an infinite sheet embedded between two semi-infinite solids, as would be useful in studies of experimentally very interesting tri-layer systems. The main difficulty then will be that the asymptotic behaviour of the wavefunction at a given energy will be a superposition of all bulk states with a given $k_{\parallel}$ and that energy, instead of the two solutions which contribute in the one-dimensional case discussed here. But we expect that the concept of transfer matrices will still apply, although the implementation of the boundary conditions will be more complicated.

Acknowledgment

Appendix A

In this appendix we rederive the KKR equation using a reference system different from the vacuum. The approach used here is very similar to the original one taken by Andersen *et al* [1]; see also reference [16]. Instead of using j_L and h_L which are the regular and irregular solutions to the free one-dimensional Schrödinger equation as given in section 2, we use now

$$z_L(E, x_i) = t_L^r(E)^{-1} j_L(E, x_i) - \frac{i}{\sqrt{E}} h_L(E, x_i) \tag{A.1}$$

and j_L, which are the regular and irregular single-site solutions (in the interstitial region) in the presence of some reference potential, to write down the wavefunction in the interstitial region near some site of the potential chain. t^{r} is the scattering matrix (t-matrix) describing the single-site contributions to this reference potential, where we assume the single-site potentials to be symmetric, t thus being diagonal. That is, we write

$$\Psi(E, x) = \sum_{L=0}^{1} \alpha_L^i z_L(E, x_i) + \sum_{L=0}^{1} \beta_L^i j_L(E, x_i) \tag{A.2}$$

for x being in the interstitial region around the ith scatterer. The sum runs over the symmetric ($L = 0$) and antisymmetric ($L = 1$) part of the wavefunction. The relation between α and β is then given by the requirement that the smooth continuation of Ψ to the region of the *physical* potential is a regular function at the origin. This results in a linear relationship between α and β. In order to express this relationship in terms of the t-matrix corresponding to the potential V_i, we re-express z in the above equation (A.2) in terms of the free solutions j and h (see equation (A.1)):

$$\Psi(E, x) = \sum_{L}(\beta_L^i + t_L^{\mathrm{r}}(E)^{-1}\alpha_L^i)j_L(E, x_i) - \frac{\mathrm{i}}{\sqrt{E}}\sum_{L}\alpha_L^i h_L(E, x_i). \tag{A.3}$$

As the coefficients in this equation are directly related to the definition of the t-matrix, we can immediately read off

$$-\frac{\mathrm{i}}{\sqrt{E}}\alpha_L^i = \frac{1}{\mathrm{i}\sqrt{E}}t_L(E)(\alpha_L t_L^{\mathrm{r}}(E)^{-1} + \beta_L) \tag{A.4}$$

which yields the linear relation

$$\beta_L = (t_L(E)^{-1} - t_L^{\mathrm{r}}(E)^{-1})\alpha_L \tag{A.5}$$

that we were looking for. Introducing the abbreviation

$$\delta m_L = t_L^{-1} - (t_L^{\mathrm{r}})^{-1} \tag{A.6}$$

the result finally reads

$$\beta_L = \delta m_L \alpha_L \tag{A.7}$$

where the site index has been suppressed.

So far, the wavefunction equation (A.2) has been defined separately for the neighbourhood of every scatterer and thus, in general, will be discontinuous at the cell boundaries. However, Ψ can also be expanded in the form

$$\Psi(E, x) = \sum_{i}\sum_{L} c_L^i h_L(E, x_i) \tag{A.8}$$

which is valid throughout the whole interstitial region. Ψ expressed by this *ansatz* is automatically differentiable at the cell boundaries due to the differentiability of the functions $h_L(E, x_i)$, and furthermore fulfils the correct boundary conditions at infinity. The KKR equation can now be derived from demanding that equation (A.2) (which guarantees the differentiability at the muffin-tin radius) and (A.8) describe the same wavefunction. To compare the two representations for x in the vicinity of the ith scatterer, the irregular functions $h_L(E, x_j)$ for $j \neq i$ can be expanded in terms of the regular functions $j_L(E, x_i)$ centred at the site i with the structure constants $g_{LL'}^{ij}$ as expansion coefficients:

$$\Psi(E, x) = \sum_{L} c_L^i h_L(E, x_i) + \mathrm{i}\sqrt{E}\sum_{j}\sum_{LL'} j_L(E, x_i)g_{LL'}^{ij}(E)c_{L'}^j. \tag{A.9}$$

This expansion of the wavefunction can be easily converted into an expansion in terms of the functions z and j:

$$\Psi(E, x) = i\sqrt{E} \sum_L c_L^i z_L(E, x_i) + i\sqrt{E} \sum_j \sum_{LL'} c_{L'}^j (g_{L'L}^{ji}(E) - \delta_{ij}\delta_{LL'} t_L^r(E)^{-1}) j_L(E, x_i).$$

(A.10)

Comparing the expressions equation (A.2) and equation (A.10) leads to

$$\alpha = i\sqrt{E}c$$
$$\beta = i\sqrt{E}(g - (t^r)^{-1})c$$

(A.11)

where we have switched over to matrix notation. Combining this with equation (A.6) and eliminating c, we get an equation determining β:

$$(g - (t^r)^{-1})(\delta m)^{-1}\beta = \beta.$$

(A.12)

Here the inverse of the scattering path matrix $\tau^r = ((t^r)^{-1} - g)^{-1}$ of the reference system appears; hence we can write

$$M\beta = 0$$

(A.13)

with the matrix

$$M = \tau^r + (\delta m)^{-1}.$$

(A.14)

This is the KKR equation in its screened form written with all indices in equation (10).

Appendix B

The aim of this appendix is to show that the wavefunction

$$\tilde{\psi}(k, x) = \left(1 - \frac{1}{\mathcal{N}}\frac{d\delta}{dk}\right)\psi(k, x)$$

(B.1)

with the periodicity length $\mathcal{N}$, is properly normalized if $\psi(E, x)$ is normalized such that asymptotically it has the same amplitude as the normalized homogeneous solution. The normalization of the homogeneous solution is an easy numerical task, since due to the periodicity a spatial integral over a unit cell is all that one has to perform. The proof given here is a generalization of Sugiyama's proof [14] for asymptotically free wavefunctions.

Using the Schrödinger equation, the norm of a wavefunction can be expressed as

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, dx = \frac{1}{2}\left(\frac{\partial E}{\partial k}\right)^{-1}\left[\frac{\partial \psi}{\partial k}\frac{\partial \psi^*}{\partial x} - \psi^*\frac{\partial^2 \psi}{\partial k \, \partial x}\right]_{x_1}^{x_2}$$

(B.2)

where x_1, x_2 are the lower and upper bounds respectively of the normalization interval. It is convenient to write ψ given in equation (9) in the form

$$\psi(x) = \sum_L b_L^j \phi_L(x_j)$$

(B.3)

with j labelling the unit cell in which x is located. Let x_1 be the left boundary of cell j_1 and x_2 the left boundary of cell j_2 with $j_2 - j_1 = \mathcal{N}$ and, by means of periodic boundary conditions, $b_L^{j_1} = b_L^{j_2}$. Equation (B.1) can then be rewritten as

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, dx = \frac{1}{2}\left(\frac{\partial E}{\partial k}\right)^{-1} \sum_{LL'}\left\{ b_L^* \frac{\partial b_{L'}}{\partial k}\bigg|_{j_1}^{j_2}\left(\frac{\partial \phi_L^*}{\partial x}\phi_{L'} - \phi_L^*\frac{\partial \phi_{L'}}{\partial x}\right)_{x=-a/2} \right.$$
$$\left. + b_L^* b_{L'}\bigg|_{j_1}^{j_2}\left(\frac{\partial \phi_L^*}{\partial k}\frac{\partial \phi_{L'}}{\partial x} - \phi_L^*\frac{\partial^2 \phi_{L'}}{\partial k \, \partial x}\right)_{x=-a/2} \right\}.$$

(B.4)

Note that all expressions containing ϕ are evaluated at the left cell boundary $x = -a/2$ (a is the lattice constant) and are site independent for sites in the asymptotic regime. Now, the terms proportional to $b_L^* b_{L'}$ are the same on both sides of the normalization interval and thus cancel each other. Because the normalization integral is a real number, one can add the complex conjugate expression and then divide by two, which yields after some rearrangement

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, dx = \frac{1}{4}\left(\frac{\partial E}{\partial k}\right)^{-1} \sum_{LL'} \left[b_L^* \frac{\partial b_{L'}}{\partial k} - \frac{\partial b_L^*}{\partial k} b_{L'} \right]_{j_1}^{j_2} W_{LL'} \tag{B.5}$$

with the abbreviation

$$W_{LL'} = \left(\frac{\partial \phi_L^*}{\partial x} \phi_{L'} - \phi_L^* \frac{\partial \phi_{L'}}{\partial x} \right)_{x=-a/2} = -W_{L'L}^*. \tag{B.6}$$

This Wronskian $W_{LL'}$ is a pure single-site quantity and is furthermore the same for all sites in the asymptotic regime. The derivatives with respect to k and with respect to x have now nicely separated.

Now, in order to proceed, more explicit expressions for the coefficients b_L have to be used. But before dealing with the general expressions we turn to the special case of the symmetric potential chain which is less troublesome and includes the important special case of the homogeneous potential chain. For the symmetric solution, the b_L are given by the equations (23) and (24) together with equation (13), and the corresponding derivatives are readily found to be

$$\frac{\partial b_0}{\partial k} = \frac{\partial(\delta m_0 \, v_0)}{\partial k} \frac{b_0}{\delta m_0 \, v_0} - \sqrt{2}\, \delta m_0 \, v_0 \sin(k|i| + \delta_0)(|i| + \delta_0')$$

$$\frac{\partial b_1}{\partial k} = \frac{\partial(\delta m_1 \, v_1)}{\partial k} \frac{b_1}{\delta m_1 \, v_1} - \operatorname{sgn} j \sqrt{2}\, \delta m_1 \, v_1 \cos(k|i| + \delta_0)(|i| + \delta_0'). \tag{B.7}$$

The primes on the phase shifts δ denote derivatives with respect to k. As m_L and v_L and their k-derivatives are the same for every site in the asymptotic regime, the first terms in the two expressions do not contribute to equation (B.5). Furthermore, the terms with $L = L'$ in the sum in equation (B.5) are zero because $b_L \, \partial b_L^*/\partial k$ is real. The remaining terms are

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, dx = \frac{1}{2}\left(\frac{\partial E}{\partial k}\right)^{-1} \left[(|j| + \delta_0') \operatorname{sgn} j\right]_{j_1}^{j_2} v_0 v_1 \left\{ -\delta m_0^* \delta m_1 \, W_{01} + \delta m_1^* \delta m_0 \, W_{10} \right\}$$

$$= \left(\frac{\partial E}{\partial k}\right)^{-1} (\mathcal{N} + 2\delta_0') v_0 v_1 \Re\{-\delta m_0^* \delta m_1 \, W_{01}\}. \tag{B.8}$$

As (v_0, v_1) are determined such that the homogeneous solution ($\delta_0' = 0$) is properly normalized, it follows that

$$\left(\frac{\partial E}{\partial k}\right)^{-1} \mathcal{N} v_0 v_1 \Re\{-\delta m_0^* \delta m_1 \, W_{01}\} = 1. \tag{B.9}$$

And therefore

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, dx = 1 + 2\frac{\delta_0'}{\mathcal{N}} = \left(1 - \frac{\delta_0'}{\mathcal{N}}\right)^{-2}. \tag{B.10}$$

This immediately implies equation (B.1) if $d\,\delta k/dk \ll 1$ is used. For the antisymmetric solution, the same equation results, with δ_0 replaced by δ_1.

In order to deal with the general case, we first establish an expression for the distance between two neighbouring k-points allowed by the boundary conditions. Equation (38) which determines the allowed k-values can be written in the form

$$\alpha(k) - \beta(k)e^{ik\mathcal{N}} = 0 \qquad \beta(k)^* - \alpha(k)^* e^{ik\mathcal{N}} = 0 \tag{B.11}$$

with

$$\alpha(k) = A_0 - iA_1 + iB_0 + B_1 \qquad \beta(k) = A_0 - iA_1 - iB_0 - B_1 \qquad \text{(B.12)}$$

where A_L, B_L are real. Equation (40) implies

$$|\alpha(k)|^2 = |\beta(k)|^2 = A_0^2 + A_1^2 + B_0^2 + B_1^2 = 1 \qquad \text{(B.13)}$$

where the last equality can be achieved by simultaneous scaling of A_0, A_1, B_0 and B_1. We will see at the end that this setting ensures the proper asymptotic behaviour. Now let k_1 and $k_2 = k_1 + \Delta k$ both fulfil equation (B.11). According to the discussion in section 4, k_1 can be written as $k_1 = i_1 2\pi/\mathcal{N} + \delta k_1$. k_2 is assumed to be the next bigger allowed k-value, i.e. $k_2 = (i_1 + 1)2\pi/\mathcal{N} + \delta k_2$. Therefore,

$$\mathcal{N} \Delta k = 2\pi + \Delta\phi \qquad \text{with } \Delta\phi = 2\pi \frac{(\delta k_2 - \delta k_1)}{2\pi/\mathcal{N}} = 2\pi \frac{\mathrm{d}\,\delta k}{\mathrm{d}k} = -\frac{4\pi}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k} \qquad \text{(B.14)}$$

and

$$2\pi \gg \Delta\phi \gg \Delta k \gg \frac{\Delta\phi}{\mathcal{N}} \qquad \text{(B.15)}$$

which can be achieved by choosing $\mathcal{N}$ big enough. Writing down the first of equations (B.11) for $k = k_2$, expanding $\alpha(k_2)$ and $\beta(k_2)$ around k_1, expanding furthermore the exponential $\exp(i(k + \Delta k)\mathcal{N}) = (1 + i\,\Delta\phi)\exp(ik\mathcal{N})$ and using $\exp(ik_1\mathcal{N}) = \alpha(k_1)/\beta(k_1)$ yields

$$\frac{\Delta\phi}{\Delta k} = i\left(\frac{\beta'}{\beta} - \frac{\alpha'}{\alpha}\right) \qquad \text{(B.16)}$$

with the prime denoting taking the derivative with respect to k. As only the leading order is of interest here, Δk may now be set to $2\pi/\mathcal{N}$. Using equation (B.14) then yields

$$\frac{\mathrm{d}\delta}{\mathrm{d}k} = -\frac{i}{2}\left(\frac{\beta^*\beta'}{|\beta|^2} - \frac{\alpha^*\alpha'}{|\alpha|^2}\right) \qquad \text{(B.17)}$$

and, with equation (B.12) and equation (40),

$$\frac{\mathrm{d}\delta}{\mathrm{d}k} = -(A_0 B_0' - A_0' B_0 + A_1 B_1' - B_1 A_1'). \qquad \text{(B.18)}$$

Now we are going to evaluate equation (B.5) for the general case where the coefficients b are given by equations (33) and (13):

$$b_0 = \sqrt{2}\,\delta m_0\, v_0((A_0 - \operatorname{sgn} j\, B_1)\cos(kj) + (A_1 + \operatorname{sgn} j\, B_0)\sin(kj))$$
$$b_1 = \sqrt{2}\,\delta m_1\, v_1((-A_0 + \operatorname{sgn} j\, B_1)\sin(kj) + (A_1 + \operatorname{sgn} j\, B_0)\cos(kj)) \qquad \text{(B.19)}$$

and the derivatives with respect to k read

$$\frac{\partial b_0}{\partial k} = \frac{\partial(\delta m_0\, v_0)}{\delta k}\frac{b_0}{\delta m_0\, v_0} + \sqrt{2}\,\delta m_0\, v_0\left\{\cos(kj)\left(\frac{\partial}{\partial k}(A_0 - \operatorname{sgn} j\, B_1) + j(A_1 + \operatorname{sgn} j\, B_0)\right)\right.$$
$$\left. + \sin(kj)\left(\frac{\partial}{\partial k}(A_1 + \operatorname{sgn} j\, B_0) - j(A_0 - \operatorname{sgn} j\, B_1)\right)\right\} \qquad \text{(B.20)}$$

$$\frac{\partial b_1}{\partial k} = \frac{\partial(\delta m_1\, v_1)}{\delta k}\frac{b_1}{\delta m_1\, v_1} + \sqrt{2}\,\delta m_1\, v_1\left\{\sin(kj)\left(\frac{\partial}{\partial k}(-A_0 + \operatorname{sgn} j\, B_1) - j(A_1 + \operatorname{sgn} j\, B_0)\right)\right.$$
$$\left. + \cos(kj)\left(\frac{\partial}{\partial k}(A_1 + \operatorname{sgn} j\, B_0) + j(-A_0 + \operatorname{sgn} j\, B_1)\right)\right\}. \qquad \text{(B.21)}$$

For the same reasons as discussed for the symmetric potential chain, the terms containing $\partial(\delta m_1\, v_1)/\delta k$ do not contribute to equation (B.5) and neither do $L = L'$ terms. Thus the relevant term is

$$\left[b_0^* \frac{\partial b_1}{\partial k} - \frac{\partial b_1^*}{\partial k} b_0\right]_{j_1}^{j_2}$$

which after some algebra is found to read

$$\left[b_0^* \frac{\partial b_1}{\partial k} - \frac{\partial b_1^*}{\partial k} b_0 \right]_{j_1}^{j_2} = -2v_0 v_1 \, \delta m_0^* \, \delta m_1 \, \mathcal{N} \left(1 + \frac{2}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k} \right). \tag{B.22}$$

And finally the normalization integral is obtained as

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, \mathrm{d}x = \left(\frac{\partial E}{\partial k} \right)^{-1} \mathcal{N} v_0 v_1 \left(1 + \frac{2}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k} \right) \Re\{ -\delta m_0^* \, \delta m_1 \, W_{01} \}. \tag{B.23}$$

Comparing the part of this expression which scales with $\mathcal{N}$ with the normalization for the homogeneous solution equation (B.9) shows that the asymptotic part of ψ is properly normalized. Thus, setting $A_0^2 + A_1^2 + B_0^2 + B_1^2 = 1$ in equation (B.13) is now justified and we finally find

$$\int_{x_1}^{x_2} |\psi(x)|^2 \, \mathrm{d}x = \left(1 + \frac{2}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k} \right) \approx 1 \Big/ \left(1 - \frac{1}{\mathcal{N}} \frac{\mathrm{d}\delta}{\mathrm{d}k} \right)^2 \tag{B.24}$$

which implies equation (B.1).

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