Wannier functions for the Kronig-Penney model

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Explicit Wannier functions for the Kronig-Penney model are determined. In the discussion we emphasize phase choices connected with maximally localized Wannier functions, here denoted Wannier-Kohn functions, and the tight-binding limit of Wannier-Kohn functions that do not approach atomic bound states.

I. INTRODUCTION

The eigenfunctions of the Schrödinger equation with a periodic potential are the Bloch wave functions $\psi_{n\mathbf{k}}(x)$, characterized by the wave number $\mathbf{k}$ and the band index n. An equivalent set of functions are the Wannier functions[1] $W_n(\mathbf{r}-\mathbf{R})$, defined in terms of the Bloch functions as

$$W_n(\mathbf{r}-\mathbf{R}) = \frac{1}{v(\mathrm{BZ})}\int_{\mathrm{BZ}} d\mathbf{k}\ \psi_{n\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{R}}. \tag{1}$$

The integration goes over the first Brillouin zone (BZ), of volume $v(\mathrm{BZ})$. There exists, for each band n, a set of Wannier functions, all identical except for simple translations through lattice vectors $\mathbf{R}$.

The Wannier functions are not eigenfunctions of the Hamiltonian, but are nevertheless useful for many theoretical discussions. The usefulness stems from the fact that the Wannier functions $W_n(\mathbf{r}-\mathbf{R})$, in contradistinction to the Bloch functions, are to some degree *localized* near the atomic sites $\mathbf{R}$.

The Wannier functions centered around different lattice points form a complete set, which is orthogonal in the sense that

$$\int d\mathbf{r}\ W_n^*(\mathbf{r}-\mathbf{R})W_{n'}(\mathbf{r}-\mathbf{R}') = \delta_{nn'}\delta_{\mathbf{R}\mathbf{R}'}. \tag{2}$$

The normalization in (2) presupposes that the Bloch functions are normalized in a unit cell of the lattice:

$$\int_{\mathrm{cell}} d\mathbf{r}\ |\ \psi_{n\mathbf{k}}(\mathbf{r})\ |^2 = 1. \tag{3}$$

In spite of the apparently simple definition (1), the properties of the Wannier functions are not obvious, and there are, we believe, questions that deserve to be elucidated. Some of these questions are the following.

(i) In the tight-binding limit the Wannier function $W_n(\mathbf{r})$ of the nth band is supposed to approach the nth atomic orbital $\chi_n(\mathbf{r})$, ordered by the energy value. What happens to the higher Wannier functions in this limit when merely one (say) atomic orbital exists, as the situation is for a one-dimensional periodic lattice of δ functions?

(ii) It is known (although often not mentioned[2,3]) that Eq. (1) does not provide a unique definition of the Wannier functions, since a Bloch function is merely determined up to an arbitrary (position-independent, but wave-vector-dependent) phase. How much does the form of a Wannier function depend upon the phase choice? Although all types of Wannier functions yield a complete set, their form matters in all computational schemes where strongly localized Wannier functions are assumed.

Explicit Wannier functions are seldom seen, and we thought it worthwhile to evaluate them for an exactly solvable model, viz., the Kronig-Penney model.[4] In addition, we find this setting useful for discussing the more general questions listed above.

II. WANNIER FUNCTIONS

The Hamiltonian for the one-dimensional Kronig-Penney model with lattice constant a and δ wells at

$$x_\nu = (\nu - \tfrac{1}{2})a, \qquad \nu = \text{integer}, \tag{4}$$

can be parametrized as follows:

$$H = \frac{p^2}{2m} - \frac{\hbar^2\alpha}{ma}\sum_\nu \delta(x - x_\nu). \tag{5}$$

The Schrödinger equation has Bloch functions

$$\psi_{nk}(x) = e^{ikx}\ u_{nk}(x) \tag{6}$$

as solutions. Between the δ wells the wave function satisfies the free-particle Schrödinger equation, and the general solution is easily written down. For positive energies,

$$E \equiv \frac{\hbar^2 q^2}{2ma^2} \geq 0, \tag{7}$$

we have in the central interval $-a/2 < x \leq a/2$,

$$\psi_{nk}^{(0)}(x) = A[\cos(ka/2)\ \sin(q/2)\ \cos(qx/a) + i\ \sin(ka/2)\ \cos(q/2)\ \sin(qx/a)]. \tag{8}$$

Here k and q are connected via the "dispersion relation"

$$\cos(ka) = \cos q - \alpha q^{-1} \sin q. \tag{9}$$

This relation, with k real, determines the allowed energies. The bottom of the nth band corresponds to $q = n\pi$ $(n = 1, 2, 3, \ldots)$. For n even, the lower band edge corresponds to $k = 0$; for n odd, to $k = \pi/a$.

The lowest (zeroth) band can have negative energies, which corresponds to purely imaginary q in the formulas above. With $E \equiv -\hbar^2 q^2/2ma^2 < 0$, the trigonometric functions are replaced by the corresponding hyperbolic functions and we have

$$\psi_{0k}^{(0)}(x) = A[\cos(ka/2)\ \sinh(q/2)\ \cosh(qx/a) + i\ \sin(ka/2)\ \cosh(q/2)\ \sinh(qx/a)]. \tag{10}$$

In both cases the Bloch functions in another interval $x_\nu < x \leq x_{\nu+1}$ are given by

$$\psi_{nk}^{(\nu)}(x) = e^{ik\nu a}\ \psi_{nk}^{(0)}(x - \nu a). \tag{11}$$

The modulus of the constant A in Eqs. (8) and (10) is determined by the normalization (3):

$$\frac{4}{a}|A|^{-2} = \begin{cases} \sin^2 q - \alpha q^{-2} \sin q\ (\sin q - q \cos q) & \text{for } E \geq 0\ , \\ \sinh^2 q + \alpha q^{-2} \sinh q\ (\sinh q - q \cosh q) & \text{for } E < 0. \end{cases} \tag{12}$$

The Wannier functions are given by

$$W_n(x) = \frac{a}{2\pi} \int_{-\pi/a}^{\pi/a} dk\ \psi_{nk}(x). \tag{13}$$

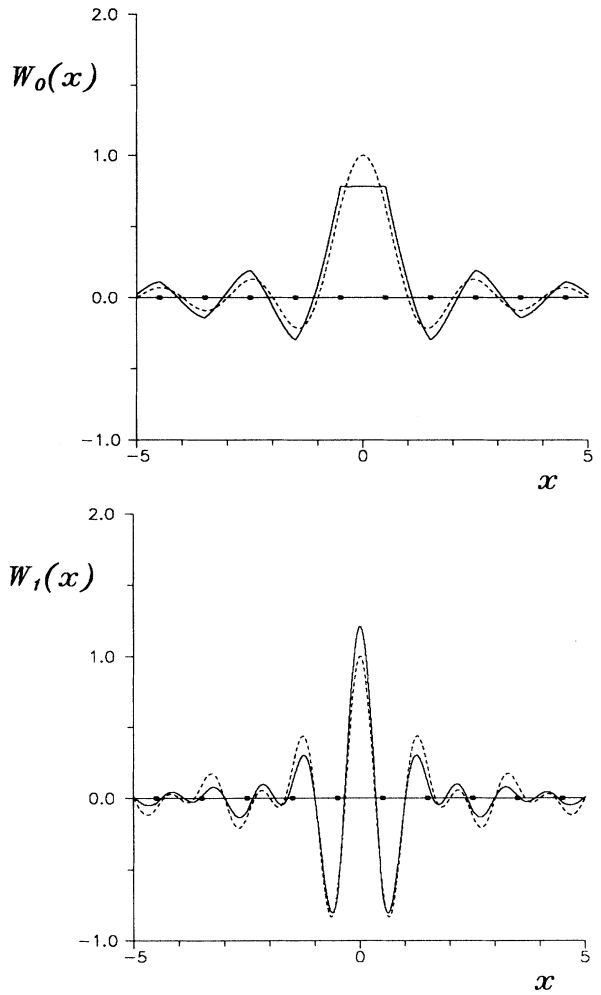

FIG. 1. The two lowest Wannier functions with the phase choice (14) for weak potentials, $\alpha = 1$ (solid lines). The corresponding free-particle Wannier functions (15) are also shown (dashed). The flat top of $W_0(x)$ is related to the transition occurring near $\alpha = 1$ between a maximum at the origin for small α and local minimum for large α. The positions of the δ wells are shown as black dots. The lattice constant is used as the unit of length.

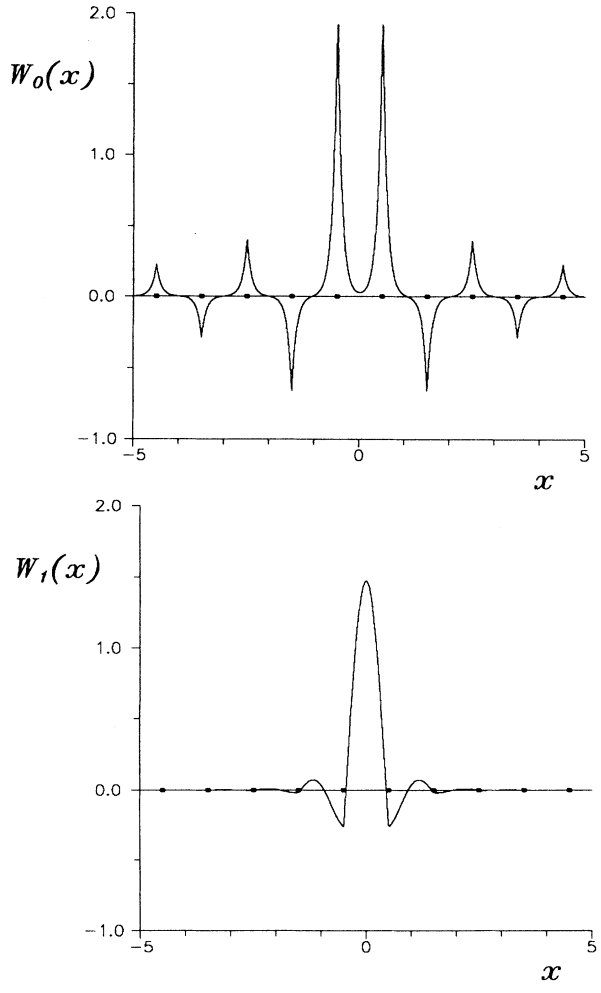

FIG. 2. The two lowest Wannier functions with the phase choice (14) for strong potentials, $\alpha = 10$.

Insertion of the Bloch functions (11), with

$$A = |A|\,, \tag{14}$$

yields a straightforward numerical integration problem.

Figure 1 shows the result for the two lowest Wannier functions for shallow δ wells, and Fig. 2 for deep wells. These Wannier functions are real and symmetric, as can easily be shown from the explicit formula.

The shallow-well results in Fig. 1 are easily interpreted as approximations to the *free-particle* Wannier functions (with the same choice of phase)

$$W_n(x) = \frac{2\sqrt{a}}{\pi x} \sin(\pi x/2a)\, \cos[(n+\tfrac{1}{2})\pi x/a]. \tag{15}$$

The deep-well results in Fig. 2 are puzzling, however. One expects in particular the lowest Wannier function $W_0(x)$ to be close to the one-well orbital

$$\chi_0(x) = (\alpha/a)^{1/2} e^{-\alpha|x|/a} \tag{16}$$

in this tight-binding limit. Instead, we observe a series of peaks of similar form but with decreasing amplitudes. Quantitatively the relative amplitudes c_n of these satellites are falling off roughly inversely proportional to their distance from the origin. That is, the relative amplitudes on the right-hand side of the origin behave as

$$1,\ -\tfrac{1}{3},\ \tfrac{1}{5},\ -\tfrac{1}{7},\ \ldots\ . \tag{17}$$

We will show below that this phenomenon, including the quantitative result (17), is not peculiar for the Kronig-Penney model, but occurs more generally. Let us, however, first see how Wannier functions can be constructed such that $W_0(x)$ does approach the "atomic" orbital $\chi_0(x)$ in the tight-binding limit.

III. WANNIER-KOHN FUNCTIONS

For a given solid there exist many sets of Wannier functions, since one is free to choose k-dependent phase factors in the normalization of the Bloch functions. As a simple example, choosing A in Eqs. (8) and (10) not real, but as

$$A = e^{-ika/2}\,|A|, \tag{18}$$

has a dramatic effect on the Wannier functions (see Figs. 3 and 4). *Now*, the Wannier function $W_0(x)$ in Fig. 4 seems to approach the "atomic" eigenfunction (16) in the tight-binding limit.

The difference between the two alternatives is easily illustrated by means of the lowest-order tight-binding form of the Bloch function (nonoverlapping atomic orbitals, normalized to unity). A natural choice of a tight-binding Bloch function, with atomic sites at $x_\nu = (\nu+\frac{1}{2})a$, is

$$\psi_{nk}(x) = \sum_{\nu=-\infty}^{\infty} e^{ikx_\nu}\, \chi_n(x - x_\nu). \tag{19}$$

The corresponding Wannier function is

$$W_n(x) = \frac{a}{2\pi} \sum_\nu \int_{-\pi/a}^{\pi/a} dk\, e^{ikx_\nu}\, \chi_n(x - x_\nu)$$
$$= \sum_\nu c_\nu \chi_n(x - x_\nu) \tag{20}$$

with

$$c_\nu = \frac{2}{\pi}\frac{(-1)^\nu}{2\nu+1}. \tag{21}$$

Multiplying (19) with the phase factor $e^{-ika/2}$, as in (18), yields instead the $c_\nu = \delta_{\nu 0}$, i.e.,

$$W_n(x) = \chi_n(x - x_0). \tag{22}$$

We see that the tight-binding result (20) and (21), in agreement with the observation (17) based on Fig. 1, is

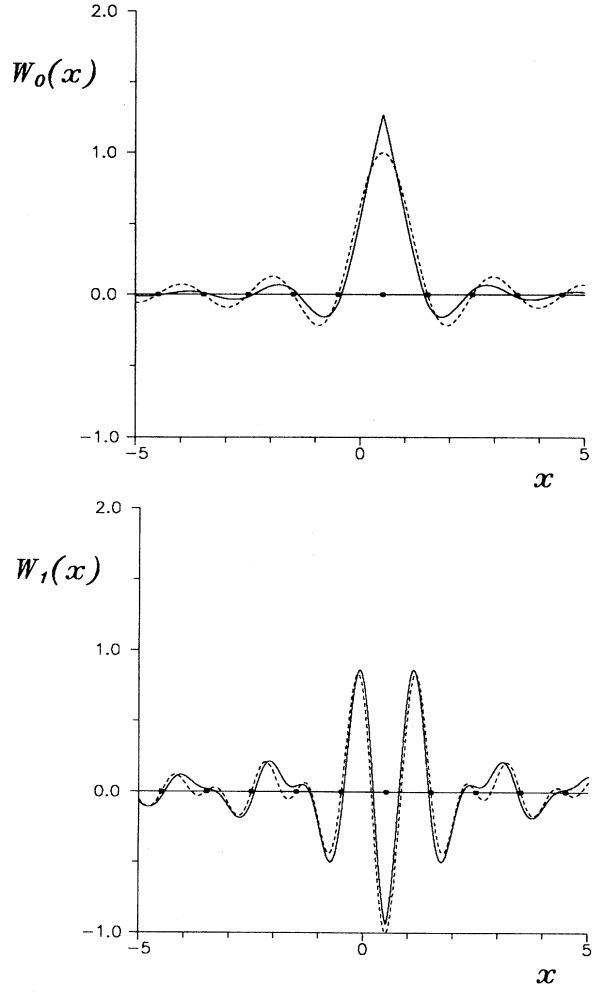

FIG. 3. The same as Fig. 1, but with the phase choice (18).

not associated with the Kronig- Penney model. It is general for one-dimensional potentials, and associated with a phase choice in the normalization. Note that

$$\sum_{\nu=-\infty}^{+\infty} c_\nu c_{\nu+\mu} = \delta_{\mu 0}, \tag{23}$$

as required by the orthonormality condition (2).

Our findings exemplify the fundamental investigations by Kohn[5] on one-dimensional periodic potentials symmetric with respect to the origin. Kohn proves that for each band there exists a unique real Wannier function $W_n(x)$ that falls off exponentially when $x \to \pm\infty$. Furthermore, $W_n(x)$ is symmetric or antisymmetric with respect to either $x = 0$ or $x = a/2$. This unique Wannier function in the set of all Wannier functions for the system we denote the *Wannier-Kohn function* for the band in question.

The recipe for constructing the Wannier-Kohn functions is simple.[5] First of all, Bloch functions $\psi_{nk}(x)$ analytic in the wave vector k should be used. Second, one should consider the values of $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$. There are three alternatives. (i) If $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$ both are nonzero, the phase of the Bloch function must be chosen such that $\psi_{nk}(0)$ is real. (ii) If both $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$ vanish, the phase must be chosen such that $\psi_{nk}(0)$ is purely imaginary. (iii) If merely one of $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$ vanishes, one can shift the origin in x space by one-half lattice constant. With respect to the new origin one will then be back to case (i) or (ii).

When applying this phase prescription to the Kronig-Penney Bloch functions (8) and (10) one must also take into account the possibility that the normalization constant $|A|^{-2}$ vanishes at the band edges. In fact, $|A|^{-2}$ vanishes at all lower band edges (where q is a multiple of π), except in the lowest band.

In the zeroth band $\psi_{n0}(0) \neq 0$, but $\psi_{n,\pi/a}(0) = 0$, i.e., case (iii). By a shift of the origin, $x \to x + \frac{1}{2}a$, we obtain for positive energies

$$\psi_{nk}^{(0)} = \frac{A}{2} e^{ika/2} [\sin q \cos(qx/a) - (e^{-ika} - \cos q) \sin(qx/a)]. \tag{24}$$

Now $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$ both are nonzero, and the choice (18), $A = e^{-ika/2}|A|$, makes $\psi_{nk}(0)$ real and $\psi_{nk}(x)$ analytic in k. The same holds for $E < 0$. Hence this choice makes the Bloch function the proper input to construct the Wannier-Kohn function $W_0(x)$, as expected from Fig. 4.

For the higher bands it is necessary to distinguish between odd and even band index n. Since from Eq. (8)

$$\psi_{nk}^{(0)}(0) = A \cos(ka/2) \sin(q/2), \tag{25}$$

we see that for n odd (when the upper band edge corresponds to $k = 0$) both $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$ will be nonzero. (To show the latter involves evaluating a 0/0 expression.) In this case we consequently take $A = |A|$. The corresponding Wannier-Kohn functions are easily seen to be real and symmetric in x.

For n even we find that both $\psi_{n0}(0)$ and $\psi_{n,\pi/a}(0)$ vanish. The recipe requires A to be purely imaginary, and it is tempting to take $A = i|A|$. This is incorrect, however, since the resulting Bloch function will then not be analytic in k at $k = 0$. (The basic reason is that $|A| \propto 1/|k|$ near $k = 0$.) The correct choice in the first Brillouin zone is

$$A = -i|A| \operatorname{sgn}(k), \tag{26}$$

with an arbitrary overall sign. Now A is an odd function of k, and one sees readily from (8) that these Wannier-Kohn functions will be real and antisymmetric in x.

After these preliminaries, which we hope are useful illustrations of the subtleties of the Wannier functions, we proceed to present in Figs. 5 and 6 the Wannier-Kohn functions for the four lowest bands.

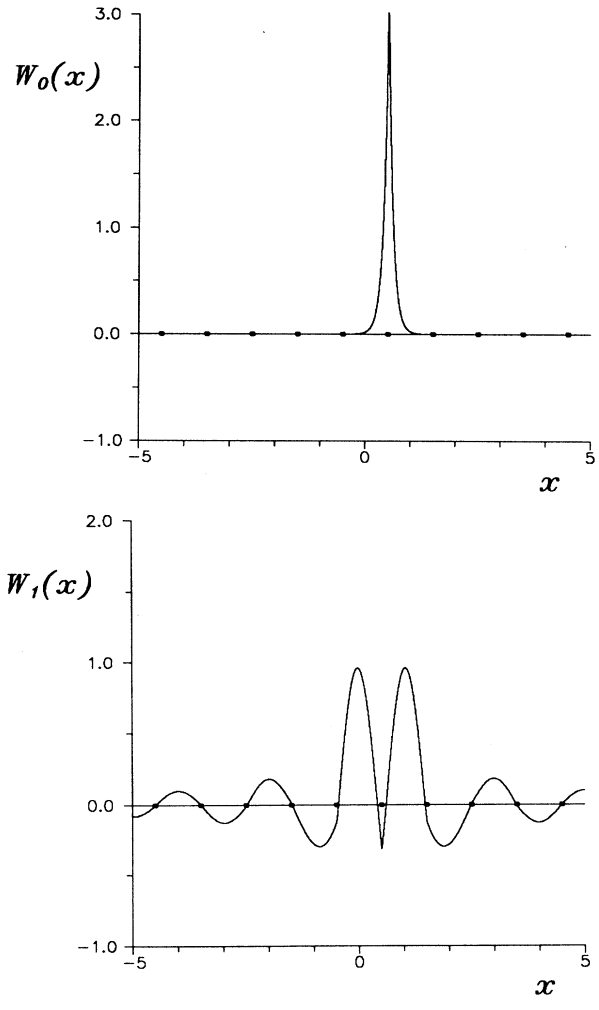

FIG. 4. The same as Fig. 2, but with the phase choice (18).

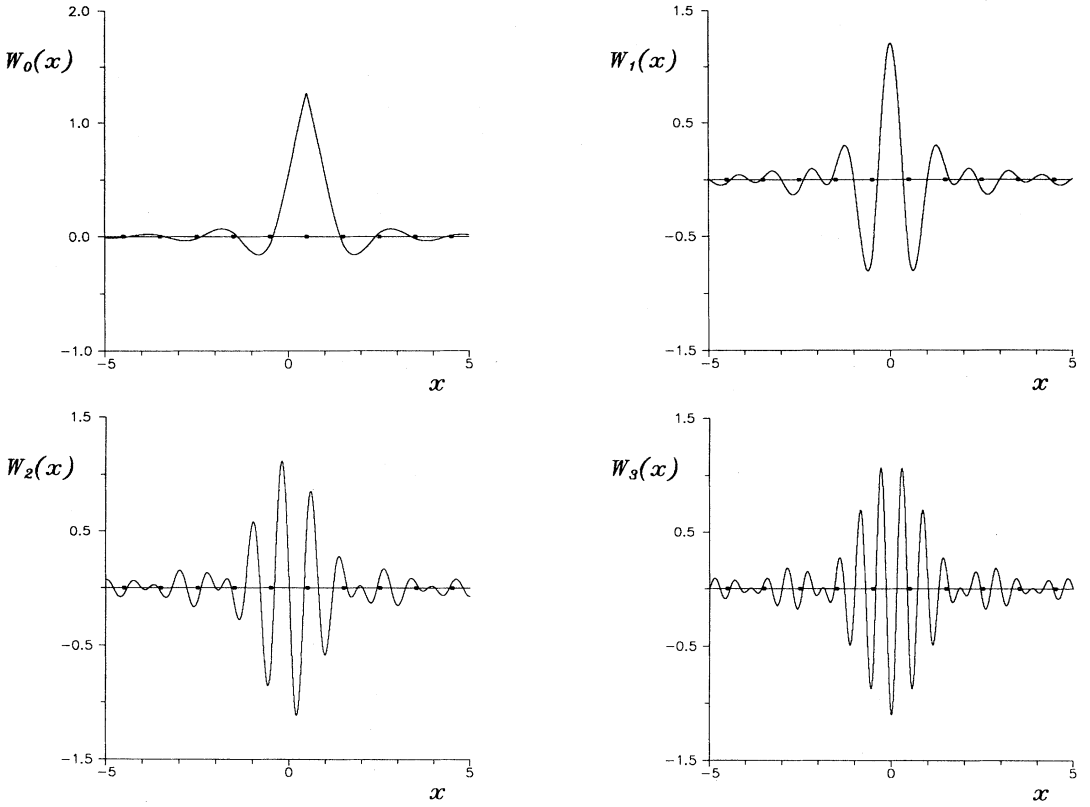

FIG. 5. Wannier-Kohn functions for the four lowest bands for weak potentials, $\alpha = 1$.

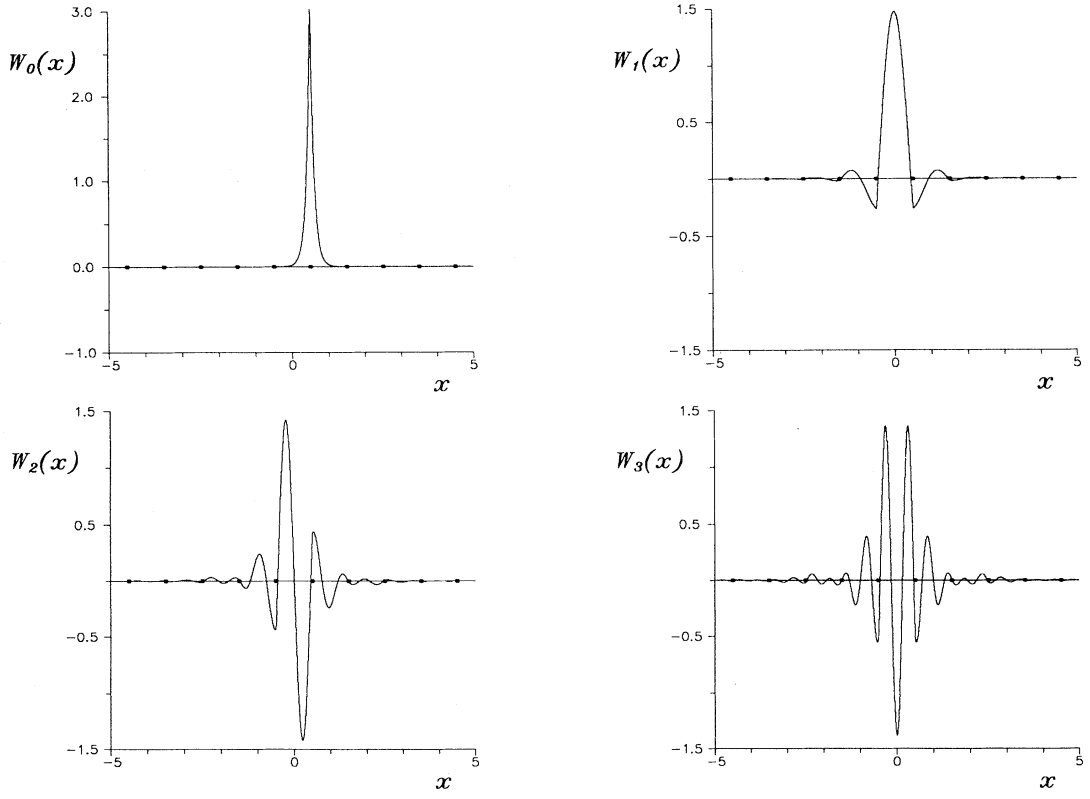

FIG. 6. Wannier-Kohn functions for the four lowest bands for strong potentials, $\alpha = 10$.

IV. TIGHT-BINDING SITUATIONS

In the extreme tight-binding limit $\alpha \to \infty$ the Wannier-Kohn function $W_0(x)$ and the atomic wave function $\chi_0(x)$ coincide, as discussed above. Their overlap,

$$t = | < W_0 | \chi_0 > |, \tag{27}$$

may be taken as a natural measure of "tightness." The tightness parameter t is shown in Fig. 7 as a function of the potential strength α.

All higher bands become exceedingly narrow and concentrated at the values $q = n\pi$ for positive energies, and it is therefore straightforward to evaluate the Wannier-Kohn functions in this limit.

For odd n we obtain

$$W_n(x) \longrightarrow \begin{cases} (2/a)^{1/2} \cos(n\pi x/a) & \text{for } |x| \leq a/2, \\ 0 \quad \text{otherwise} \end{cases} \tag{28}$$

and for even n

$$W_n(x) \longrightarrow \begin{cases} (2/a)^{1/2} \sin(n\pi x/a) & \text{for } |x| \leq a/2, \\ 0 \quad \text{otherwise.} \end{cases} \tag{29}$$

This is in qualitative agreement with Fig. 6.

For our model, in which the atomic potential carries merely one bound state, one sees that only one Wannier-Kohn function becomes extremely localized in the tight-binding limit, the others fill one lattice cell in this limit. This is no doubt a general feature.

It is not possible to draw this conclusion from the standard construction (19) of the lowest-order tight-binding Bloch function. This is not paradoxical, since atomic eigenfunctions in the continuous spectrum are not included in this construction.

Bloch functions can be composed into identical Wannier functions located at different lattice sites:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} W_n(\mathbf{r} - \mathbf{R})\, e^{i\mathbf{k}\cdot\mathbf{R}}. \tag{30}$$

This is the inversion of Eq. (1). It is interesting to note that in the tight-binding limit the Bloch functions can be built up by simply appending nonoverlapping pieces of Wannier-Kohn functions, multiplied with the appropriate exponential factor. (This is not so for other Wannier functions.)

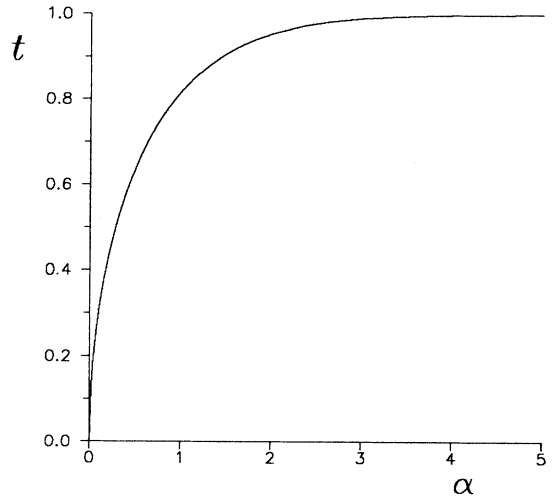

FIG. 7. The tightness parameter t (27) shown as a function of the potential strength α.

V. CONCLUDING REMARKS

Above we have illustrated, in the Kronig-Penney model, how different choices of phase factors for Bloch functions lead to Wannier functions with different properties. For the maximally localized Wannier functions, here denoted Wannier-Kohn functions, several interesting properties emerge.

Let us use the abbreviation "bound-state Wannier-Kohn function" for a Wannier-Kohn function corresponding to one of the n_0 lowest bands, where n_0 is the number of atomic orbitals for an isolated well. (For the Kronig-Penney model $n_0 = 1$.) We have then found the following properties.

(i) The bound-state Wannier-Kohn function has an atomic well as symmetry center, the other Wannier-Kohn functions are symmetric or antisymmetric with respect to midpoints between two neighboring wells.

(ii) In the tight-binding limit (strong-potential limit) the bound-state Wannier-Kohn functions approach extremely localized atomic bound-state wave functions, while the other Wannier-Kohn functions approach a nonzero limit in one unit cell and are zero outside.

These properties are probably general for one-dimensional periodic potentials.

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