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Stark ladders and Zener tunnelling

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Abstract. In connection with the controversial question about the interband matrix elements of a stair-function potential in a crystal, we show analytically that they are non-vanishing, in general, for an arbitrary band model for both an infinite and a finite crystal. This is in accord with numerical studies of specialised models, but in contradiction to other analytical claims, which are analysed in some detail. The connection to the phenomena of Stark ladders and Zener tunnelling is discussed.

1. Introduction

The motion of an electron in a periodic potential and a uniform electric field continues to be a topic of considerable current interest and controversy [1–11]. The existence and nature of the energy Stark ladders [12] and the possibility of Zener tunnelling [13] across the energy bands have been investigated by analytical and numerical mewthods [1–17].

In many numerical investigations of these questions [1, 7, 16, 17] the effect of the electric field was approximated, for numerical convenience, by a stair-function potential which increases by equal steps over each unit cell or a submultiple of the unit cell. Such a model has real significance, because the electrostatic potential of a constant electric field can be written as a sum of a periodic part with the period of the crystal—the sawtooth-function potential for a one-dimensional crystal—and the stair-function potential. The periodic part alters the shape of the periodic potential of the crystal in each unit cell and it can thus define electric-field dependent energy bands, while the stair-function potential determines the motion of the electron in these new bands.

Such a splitting was considered analytically recently [2–5] and it was claimed that for both infinite and finite crystals the stair-function potential has no interband matrix elements. A similar claim was published earlier [9] on the basis of some qualitative arguments and a conjecture based on a highly singular model of a periodic potential. This important claim has as a consequence the existence of an *exact* Stark energy ladder for each electric-field-dependent energy band, and the description of Zener tunnelling as due to the effects solely of the sawtooth-function of the electric-field potential.

In contrast, numerical studies [1, 7, 16, 17] have demonstrated that the stair-function potential has non-vanishing interband matrix elements. In the most recent such study [1], a model of two tight-binding energy bands was considered in the presence of a stair-function potential. By an interesting and careful examination of the eigenfunctions, the conclusion was reached that the stair-function potential has definitely non-vanishing

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interband matrix elements, and the resultant Zener tunnelling was discussed and estimated. In confronting the recent analytical results [5] claiming the contrary conclusion, the authors of [1] stated that there is an error in [5] and suggested the location of the mistake.

In this paper we present an analytical study of the same question for an arbitrary multiband model. We evaluate the interband matrix elements of the stair-function in terms of the values of the Bloch wavefunctions and their derivatives at the edges of the unit cell, for both an infinite and a finite crystal. These expressions show that, in general, the interband matrix elements are different from zero, in agreement with the numerical studies. Furthermore, they provide a new way for evaluating their magnitude. An examination of earlier theories [2, 3, 5, 9] claiming the opposite result is given in some detail. Finally we discuss the questions of Stark energy ladders and Zener tunnelling on the basis of these findings.

2. Stair-function potential in a crystal

We consider, as in [1–5, 7–11], one electron in a one-dimensional periodic potential $V(x)$ with period a, i.e. $V(x+a)=V(x)$, and a stair-function potential $eES(x)$, which increases by eEa on each period a of the crystal. The periodic potential $V(x)$ is arbitrary, and it may be taken to include the periodic sawtooth-function of the electric field potential eEx [5]. We shall assume, however, $V(x)$ to be finite everywhere, so that the energy eigenfunctions, given by

$$H\psi_{nk}(x) \equiv (p^2/2m + V(x))\psi_{nk}(x) = \varepsilon_{nk}\psi_{nk}(x) \tag{1}$$

where $p=(1/\mathrm{i})(\partial/\partial x)$ is the momentum operator, are continuous with continuous first derivatives, and such that the energy spectrum can be organised into bands ε_{nk}, with n denoting the band index and k the Bloch wavenumber. In (1) $\psi_{nk}(x)$ are the Bloch functions

$$\psi_{nk}(x) = \mathrm{e}^{\mathrm{i}kx}u_{nk}(x) \qquad u_{nk}(x+a)=u_{nk}(x). \tag{2}$$

We write the stair-function $S(x)$ in the form

$$S(x) = ma \qquad \text{for } ma < x < (m+1)a \tag{3}$$

where $m=0, \pm 1, \pm 2, \ldots$. We are interested in the matrix elements of $S(x)$ in the Bloch representation (2). We consider the cases of an infinite and a finite crystal separately, as the arguments differ.

2.1. *Infinite crystal*

In this case the wavenumber k is a continuous variable within the Brillouin zone $(-\pi/a, \pi/a)$. The normalisation condition

$$\langle nk|n'k'\rangle \equiv \int_{-\infty}^{+\infty} \psi^*_{nk}(x)\psi_{n'k'}(x)\,\mathrm{d}x = \delta_{nn'}\delta(k-k') \tag{4}$$

leads, through a cell-by-cell integration, to the orthonormalisation condition

$$(\psi_{nk}|\psi_{n'k}) = (u_{nk}|u_{n'k}) \equiv \int_0^a u^*_{nk}(x)u_{n'k}(x)\,\mathrm{d}x = (a/2\pi)\delta_{nn'} \tag{5}$$

where we made use of the relation

$$\sum_{m=-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}(k-k')am} = (2\pi/a)\delta(k-k'). \tag{6}$$

For the matrix elements of $S(x)$ we find, again by a cell-by-cell integration,

$$\langle nk|S|n'k'\rangle = \int_{-\infty}^{\infty} \psi_{nk}^*(x)S(x)\psi_{n'k'}(x)\,\mathrm{d}x = \sum_{-\infty}^{\infty} ma\,\mathrm{e}^{-\mathrm{i}(k-k')ma}(\psi_{nk}|\psi_{n'k'})$$

$$= \mathrm{i}\frac{\partial\delta(k-k')}{\partial k}\frac{2\pi}{a}(\psi_{nk}|\psi_{n'k'}) = \mathrm{i}\,\delta_{nn'}\frac{\partial}{\partial k}\delta(k-k') + \delta(k-k')\sigma_{nn'}(k) \qquad (7)$$

where

$$\sigma_{nn'}(k) = (2\pi/a)(\psi_{nk}|\mathrm{i}(\partial/\partial k)\psi_{n'k}) \qquad (8a)$$

$$= X_{nn'}(k) - x_{nn'}(k) \qquad (8b)$$

$$X_{nn'}(k) = (2\pi/a)(u_{nk}|\mathrm{i}(\partial/\partial k)u_{n'k}) \qquad (9a)$$

$$x_{nnn'}(k) = (2\pi/a)(u_{nk}|x|u_{n'k}). \qquad (9b)$$

In arriving at these expressions we made use of equation (5) and the usual properties of the delta-function $\delta(k-k')$ valid for integrations over k'. Equations (8–9) for $\sigma_{nn'}(k)$ are in accord with the fact that the stair-function $S(x)$ can be considered as the difference between the function x (from $-\infty$ to ∞), with interband matrix elements $X_{nn'}(k)$, and the periodic sawtooth-function defined as x within the central unit cell $(0, a)$, with interband elements $x_{nn'}(k)$.

We now evaluate $\sigma_{nn'}(k)$ in terms of the values of $u_{nk}(x)$ and its derivatives at the end points of the central unit cell $(0, a)$, on the basis of the Schrödinger equation that determines $u_{nk}(x)$. From (1) we have the usual equation defining $u_{nk}(x)$ within the unit cell $(0, a)$

$$H(k)u_{nk}(x) \equiv [(1/2m)(p+k)^2 + V(x)]u_{nk}(x) = \varepsilon_{nk}u_{nk}(x) \qquad (10)$$

with the boundary condition of periodicity $u_{nk}(x+a) = u_{nk}(x)$, as in (2). We now note first that, writing (10) with the use of (5) in the form

$$(2\pi/a)(u_{nk}|H(k)|u_{n'k}) = \varepsilon_{nk}\delta_{nn'} \qquad (11)$$

differentiating with respect to k and observing that $H(k)$ is Hermitian with respect to u_{nk}, $u_{n'k}$ over the interval $(0, a)$ due to the periodicity of $u_{nk}(x)$ and its derivatives with respect to x and k, we get

$$(1/m)(p_{nn'}(k) + k\delta_{nn'}) = (\partial\varepsilon_{nk}/\partial k)\delta_{nn'} + \mathrm{i}(\varepsilon_{nk} - \varepsilon_{n'k})X_{nn'}(k). \qquad (12)$$

Here we have put

$$p_{nn'}(k) = (2\pi/a)(u_{nk}|p|u_{n'k}) \qquad (13)$$

and made use of (9a) and $\partial H(k)/\partial k = (p+k)/m$. On the other hand we note that

$$(p+k)/m = \mathrm{i}[H(k), x] \qquad (14)$$

and upon evaluating its matrix elements by integration by parts (as $H(k)$ is not Hermitian with respect to $u_{nk}(x)$, $xu_{n'k}(x)$ over the interval $(0, a)$), we have

$$(1/m)(p_{nn'}(k) + k\delta_{nn'}) = \mathrm{i}(\varepsilon_{nk} - \varepsilon_{n'k})x_{nn'}(k) - 2\pi\,\mathrm{i}\,W_{nn'}(k, a) \qquad (15)$$

where

$$W_{nn'}(k, x) = (1/2m)(u_{nk}^*(x)\partial u_{n'k}(x)/\partial x - \partial u_{nk}^*(x)/\partial x\,u_{n'k}(x)$$

$$+ 2\,\mathrm{i}\,ku_{nk}^*(x)u_{n'k}(x)) \qquad (16)$$

using (9*b*). Comparing now (12) and (15) and recalling the definition (8) of $\sigma_{nn'}(k)$, we have for the interband matrix elements $n' \neq n$

$$\sigma_{nn'}(k) = -2\pi W_{nn'}(k, a)/(\varepsilon_{nk} - \varepsilon_{n'k}). \tag{17}$$

Clearly this method does not determine $\sigma_{nn}(k)$.

The quantity $W_{nn'}(k, x)$, (16), is easily seen to be the (modified) Wronskian for $u_{nk}(x)$, $u_{n'k}(x)$, appropriate to the differential equation (10), and clearly satisfies the differential equation

$$(\partial/\partial x)W_{nn'}(k, x) = (\varepsilon_{nk} - \varepsilon_{n'k})u^*_{nk}(x)u_{n'k}(x). \tag{18}$$

For any periodic potential $V(x)$ without infinite discontinuities, we have $W_{nn'}(k, x + a) = W_{nn'}(k, x)$ due to the continuity of $\partial u_{nk}(x)/\partial x$. This property of $W_{nn'}(k, x)$ along with (18) prove the orthogonality condition (5). For the intraband elements we have from (18) that

$$W_{nn}(k, x) = W_{nn}(k, a). \tag{19}$$

These have physical significance, since from (12) and (15) we have

$$-2\pi \,\mathrm{i}\, W_{nn}(k, a) = \partial\varepsilon_{nk}/\partial k = (1/m)(p_{nn}(k) + k). \tag{20}$$

According to (17), $\sigma_{nn'}(k)$ depends on the value of the Wronskian at the end points of the unit cell, $W_{nn'}(k, a) = W_{nn'}(k, 0)$. From (16) and (18) for $W_{nn'}(k, x)$ we see that there is no reason for it to vanish at the edges of the cell for all $n, n'(\neq n)$ and an arbitrary k. Furthermore, we note that for a fixed periodic potential, $W_{nn'}(k, a)$ depends on the choice of the unit cell. This is obvious from the definition of $\sigma_{nn'}(k)$, (9*a*), since the first term $X_{nn'}(k)$ is clearly independent of, while the second term $x_{nn'}(k)$ obviously depends on the location of $(0, a)$ with respect to the periodic potential. That is, if the unit cell is taken to be $(x_0, x_0 + a)$, then $\sigma_{nn'}(k) \propto W_{nn'}(k, x_0)$. Thus, since it is clear from (16) and (18) that $W_{nn'}(k, x)$ does not vanish everywhere on the x-axis, $\sigma_{nn'}(k) \neq 0$ $(n' \neq n)$ for an arbitrary unit cell. If, however, the periodic potential that determines the band structure is chosen to include the sawtooth-function part of x, as in [2–5], this argument may be objected to. However, no argument has been presented that claims the vanishing of $\sigma_{nn'}(k)$ specifically for such periodic potential, in view of the fact that the unperturbed crystal is described by an arbitrary periodic potential to begin with.

We can demonstrate some of these points explicitly for the extreme model of a periodic potential consisting of infinite potential walls at a distance a apart, i.e.

$$V(x) = \begin{cases} 0 & x \neq ma \quad (m = 0, \pm 1, \pm 2, \ldots) \\ \infty & x = ma. \end{cases} \tag{21}$$

The eigenfunctions and eigenvalues are

$$\psi_{nk}(x) = \mathrm{e}^{\mathrm{i}kx}u_{nk}(x) = (1/\sqrt{\pi})\sin(n\pi x/a) \qquad (0 < x < a)$$
$$\varepsilon_{nk} = (1/2m)(n\pi/a)^2 \qquad n = 1, 2, 3, \ldots. \tag{22}$$

Then, by direct evaluation of (8*a*) we have $\sigma_{nn'}(k) = 0$. Similarly, from expressions (17) and (16), we have also $\sigma_{nn'}(k) = 0$, while (20) yields $\partial\varepsilon_{nk}/\partial k = 0$, in accord with (22). We should note that although expressions (17) and (20) were derived for a finite $V(x)$ with continuous $\partial u_{nk}(x)/\partial x$, etc, they also hold true for this case because $u_{nk}(0) =$

$u_{nk}(a) = 0$ as it can be easily checked [18]. But, if we now displace the unit cell $(0, a)$ so that

$$V(x) = \begin{cases} 0 & x \neq m(a/2) \quad (m = \pm 1, \pm 2, \ldots) \\ \infty & x = m(a/2), \end{cases} \tag{23}$$

the eigenfunctions are

$$\psi_{nk}(x) = \mathrm{e}^{\mathrm{i}kx} u_{nk}(x) = \begin{cases} \dfrac{1}{\sqrt{\pi}} \sin\left[\dfrac{n\pi}{a}\left(x + \dfrac{a}{2}\right)\right] \mathrm{e}^{-\mathrm{i}ka/2} & (0 < x < a/2) \\ \dfrac{1}{\sqrt{\pi}} \sin\left[\dfrac{n\pi}{a}\left(x - \dfrac{a}{2}\right)\right] \mathrm{e}^{\mathrm{i}ka/2} & (a/2 < x < a) \\ 0 & (x = a/2) \end{cases} \tag{24}$$

with same, of course, eigenvalues $\varepsilon_{nk} = (1/2)(n\pi/a)^2$ $(n = 1, 2, 3, \ldots)$. Now by direct evaluation of $(8a)$ or by use of expression (17), we find

$$\sigma_{nn'}(k) = \frac{2a/\pi}{n^2 - n'^2}\left(n \cos\frac{n\pi}{2} \sin\frac{n'\pi}{2} - n' \sin\frac{n\pi}{2} \cos\frac{n'\pi}{2}\right) \tag{25}$$

which is non-vanishing in general.

Often one considers [9, 16] a stair-function potential that has an integral number of equal steps (a/ν) within each unit cell, i.e.

$$S^{(\nu)}(x) = m(a/\nu) \qquad \text{for} \quad m(a/\nu) < x < (m+1)(a/\nu) \tag{26}$$

where $\nu = 1, 2, 3, \ldots$ and $m = 0, \pm 1, \pm 2, \ldots$, while the period of $V(x)$ is again a. For its matrix elements we find

$$\sigma_{nn'}^{(\nu)} = \frac{2\pi}{a}\left[\left(\psi_{nk} \left| \mathrm{i}\frac{\partial}{\partial k} \psi_{n'k}\right.\right) + \sum_{m=0}^{\nu-1} m(a/\nu) \int_{m(a/\nu)}^{(m+1)(a/\nu)} u_{nk}^*(x) u_{n'k}(x)\, \mathrm{d}x\right] \tag{27}$$

$$= \frac{2\pi}{a} \int_0^a u_{nk}^*(x)\left(\mathrm{i}\frac{\partial}{\partial k} + S^{(\nu)}(x) - x\right) u_{n'k}(x)\, \mathrm{d}x. \tag{28}$$

This quantity is clearly non-vanishing, and since $S^{(\nu)}(x) \to x$ as $\nu \to \infty$ (definitely for the integral (28)), we get

$$\sigma_{nn'}^{(\infty)}(k) = (2\pi/a)(u_{nk} | \mathrm{i}(\partial/\partial k) u_{n'k}) = X_{nn'}(k) \tag{29}$$

which is the well-known interband matrix element of x, as we should.

2.2. Finite crystal

We consider now a finite crystal consisting of N unit cells in the basic domain $(0, Na)$. The Bloch functions $\psi_{nk}(x)$ are as in (2), except that now the Bloch wavenumber k is discrete assuming the N values

$$k = (2\pi/Na)s \qquad s = 0, 1, 2, \ldots, N-1. \tag{30}$$

For such values we have that $\psi_{nk}(x)$ is periodic of the basic domain Na, while the orthonormalisation conditions (4), (5) become now

$$\langle nk|n'k'\rangle \equiv \int_0^{Na} \psi^*_{nk}(x)\psi_{n'k'}(x)\,\mathrm{d}x = \delta_{nn'}\delta_{kk'} \tag{31}$$

and

$$(\psi_{nk}|\psi_{n'k}) = (u_{nk}|u_{n'k}) \equiv \int_0^a u^*_{nk}(x)u_{n'k}(x)\,\mathrm{d}x = (1/N)\delta_{nn'}. \tag{32}$$

The stair-function $S(x)$ is given, as before, by (3) except now $m = 0, 1, 2, \ldots N-1$. We thus find for the matrix elements

$$\langle nk|S|n'k'\rangle = \int_0^{Na} \psi^*_{nk}(x)S(x)\psi_{n'k'}(x)\,\mathrm{d}x = \left(\sum_{m=0}^{N-1} ma\,\mathrm{e}^{-\mathrm{i}(k-k')ma}\right)(\psi_{nk}|\psi_{n'k'}). \tag{33}$$

In order to proceed further in analogy to the case of the infinite crystal, we introduce an operation with respect to the discrete k, (30), that is in some ways analogous to the differentiation $\partial/\partial k$ in the case of a continuous k. Every function of the N ks is viewed as a N-dimensional vector in a space spanned by the complete set of the N orthonormal vectors

$$\mathrm{e}^{\mathrm{i}kra}/\sqrt{N} \qquad (r = 0, 1, 2, \ldots, N-1)$$

such that

$$(1/N)\sum_{r=0}^{N-1} \mathrm{e}^{\mathrm{i}(k-k')ra} = \delta_{kk'} \tag{34a}$$

$$(1/N)\sum_{k} \mathrm{e}^{\mathrm{i}k(r-r')a} = \delta_{rr'} \tag{34b}$$

where Σ_k goes over the N values of k indicated in (30). Thus, for any such function A_k we have

$$A_k = \sum_{r=0}^{N-1} \mathrm{e}^{\mathrm{i}kra}A(r) \tag{35a}$$

$$A(r) = \frac{1}{N}\sum_{k} \mathrm{e}^{\mathrm{i}kra}A_k. \tag{35b}$$

We now define the operation ∂_k on the basis of the definition (35a), namely

$$\partial_k A_k \equiv \sum_{r=0}^{N-1} \mathrm{i}ra\,\mathrm{e}^{\mathrm{i}kra}A(r). \tag{36}$$

It is easy to verify that ∂_k has the same properties as the ordinary differentiation $\partial/\partial k$ for functions of the continuous k for sums and products of functions

$$\partial_k(\lambda A_k + \mu B_k) = \lambda\partial_k A_k + \mu\partial_k B_k \tag{37a}$$

$$\partial_k(A_k B_k) = A_k\partial_k B_k + (\partial_k A_k)B_k. \tag{37b}$$

In addition we note the important property

$$\sum_k \partial_k A_k = 0 \tag{38}$$

which follows from (36) and (34*b*).

Now the components of the Bloch wavefunction $\psi_{nk}(x)$ are the well-known Wannier functions, i.e.

$$\psi_{nk}(x) = \mathrm{e}^{\mathrm{i}kx} u_{nk}(x) = \sum_{r=0}^{N-1} \mathrm{e}^{\mathrm{i}kar} w_n(x - ar). \tag{39}$$

From the orthonormality (31) of the ψ_{nk}s, we obtain for the Wannier functions

$$\int_0^{Na} w_n^*(x - ar) w_{n'}(x - ar')\, \mathrm{d}x = (1/N)\delta_{nn'}\delta_{rr'}. \tag{40}$$

Such a relation is possible for the $w_n(x - ar)$s, because the $w_n(x)$s have the periodicity of the basic domain Na, as $\psi_{nk}(x)$s do, as it follows from their definition (39) and (35*b*). From (39) we note that the component representation of the periodic part of the Bloch wavefunction $u_{nk}(x)$, namely

$$u_{nk}(x) = \sum_{r=0}^{N-1} \mathrm{e}^{-\mathrm{i}k(x-ar)} w_n(x - ar) \tag{41}$$

has the important feature that

$$\partial_k u_{nk}(x) = -\mathrm{i} \sum_{r=0}^{N-1} (x - ar)\, \mathrm{e}^{\mathrm{i}k(x-ar)} w_n(x - ar) \tag{42}$$

is *not* periodic in x, as it can be easily ascertained, in contrast to $\partial u_{nk}(x)/\partial k$ for the infinite crystal.

With these observations we rewrite (33) in the form

$$\langle nk|S|n'k'\rangle = -\mathrm{i}N(\partial_{k'}, \partial_{k,k'})(\psi_{nk}|\psi_{n'k'}) = \mathrm{i}N\delta_{nn'}\partial_k\delta_{k,k'} + N\delta_{k,k'}\sigma_{nn'}(k) \tag{43}$$

where

$$\sigma_{nn'}(k) = (\psi_{nk}|\mathrm{i}\,\partial_k\psi_{n'k}), \tag{44}$$

having made use of (37*b*), (38) and (32). We may evaluate (44) from the Schrödinger equation (1) for $\psi_{nk}(x)$ in the internal $(0, a)$ by performing the operation ∂_k and taking its projection onto $\psi_{nk}(x)$. We find, by integration by parts

$$(\varepsilon_{nk} - \varepsilon_{n'k})(\psi_{nk}|\partial_k\psi_{n'k}) = (1/N)\delta_{nn'}\partial_k\varepsilon_{nk} + \mathrm{i}(aW_{nn'}(k, a) + R_{nn'}(k, a) - R_{nn'}(k, 0)) \tag{45}$$

where $W_{nn'}(k, x)$ is given as before by (16) and

$$R_{nn'}(k, x) = (-\mathrm{i}/2m)(u_{nk}^*(x)\partial/\partial x - \partial u_{nk}^*(x)/\partial x + 2\,\mathrm{i}\,k u_{nk}^*(x))\partial_k u_{n'k}(x). \tag{46}$$

We thus have for $n' \neq n$

$$\sigma_{nn'}(k) = -(aW_{nn'}(k,a) + R_{nn'}(k,a) - R_{nn'}(k,0))/(\varepsilon_{nk} - \varepsilon_{n'k}). \tag{47}$$

Thus, for the finite crystal, in addition to the Wronskian $W_{nn'}(k, a)$ we discussed above in connection with the infinite crystal, there is the difference in the values of $R_{nn'}(k, x)$

at the edges of the unit cell, due to the non-periodicity of $\partial_k u_{n'k}(x)$ we noted in connection with (42). For the case of the infinite crystal $\partial_k u_{nk}(x)$ becomes $\partial u_{nk}(x)/\partial k$ and its periodicity makes the contribution of $R_{nn'}(k, x)$ in (47) vanish, thus re-establishing the earlier result. We thus conclude that for the general case for a finite crystal we have $\sigma_{nn'}(k) \neq 0$,

3. Discussion

We discuss here the various arguments that have been presented recently in the literature claiming to show, contrary to our findings, that the stair-function has no interband matrix elements, i.e. $\sigma_{nn'}(k) = 0$.

It has been argued in [9] that the replacement of x by $S(x)$ in an infinite crystal amounts to a one-band approximation. Specifically, it was recalled that the matrix elements of x in the Bloch representation [19]

$$\langle nk|x|n'k'\rangle = \mathrm{i}\,\delta_{nn'}(\partial/\partial k)\delta(k-k') + \delta(k-k')X_{nn'}(k) \tag{48}$$

where $X_{nn'}(k)$ are given by (9*a*), are such that if one ignores the interband elements $X_{nn'}(k)$ the energy spectrum of the electron is [15, 9]

$$\varepsilon_{n\nu} = eEa\nu + \langle \varepsilon_{nk} + eEX_{nn}(k)\rangle \qquad \nu = 0, \pm 1, \pm 2, \ldots \tag{49}$$

where $\langle\ \rangle$ denotes the average over the band. Thus, in this one-band approximation, there is an energy Stark ladder associated with each band n. It was then concluded [9] that this approximation (i.e. $X_{nn'}(k) = 0$) is equivalent to Schrodinger's equation in which the electric field potential is replaced by the stair-function $eES(x)$. The basis for this conclusion is *presumably* (no detailed argument was given) the fact that the spectrum of $eES(x)$ is $eEa\nu$ ($\nu = 0, \pm 1, \pm 2, \ldots$). But, this spectrum is *not* the same as in (49), since (49) is a Stark ladder for each band. It seems to us that one may not conclude on the basis of this argument that a stair-function potential $eES(x)$ on a crystal is equivalent to an electric field potential eEx in a one-band approximation.

In a more quantitative argument, it was pointed out [9] that $\sigma_{nn'}(k) = 0$ ($n' \neq n$) for the case of ultralocalised Wannier functions, i.e. for the periodic potential (21), as we noted earlier. It was then stated that a similar result is *expected* for any set of well-localised Wannier functions. It was finally *concluded* that $S(x)$ has vanishing interband matrix elements (at least for a tight-binding model). We have shown above, however, that the vanishing of $\sigma_{nn'}(k)$ for the potential (21) is not typical, and, in fact, even for the same potential $\sigma_{nn'}(k) \neq 0$ if the unit cell is chosen differently.

Furthermore, it was argued in [9] that a stair-function with a step equal to a sub-multiple of the period a, (a/ν), is again equivalent to a one-band approximation. We have shown, however, that in such a case the interband elements $\sigma_{nn'}^{(\nu)}(k)$, (28), are different from $\sigma_{nn'}(k)$ in general, and as $\nu \to \infty$ such a stair-function approaches the operator x, as it should.

We finally conclude that although $S(x)$ and x are different operators, they are quite similar in that they both have non-vanishing interband matrix elements and similar intraband elements. In fact, as the steps of $S(x)$ become smaller the effects of $S(x)$ approach those of x.

Another argument has been published recently [5] that claims to show that $\sigma_{nn'}(k) = 0$ for an arbitrary band structure and for a *finite* crystal $(0, Na)$. In [5] expression (44) for $\sigma_{nn'}(k)$ is written in the form

$$\sigma_{nn'}(k) = -(u_{nk}|x|u_{n'k}) + (u_{nk}|\mathrm{i}\,\partial_k u_{n'k}), \tag{50}$$

with the use of (37*b*) and (39). The two terms in (50) are then compared by evaluating $\langle nk|x|n'k\rangle$ in two different ways. First, by a cell-by-cell integration one finds

$$\langle nk|x|n'k\rangle = \sum_{m=0}^{N-1} \int_{ma}^{(m+1)a} \mathrm{d}x\, u^*_{nk}(x) x u_{n'k}(x) = N(u_{nk}|x|u_{n'k}) + \delta_{nn'} a(N-1)/2 \tag{51}$$

with the use of (32). Secondly, one attempts to evaluate $\langle nk|x|n'k'\rangle$ by noting, as in the standard way [19] for the infinite crystal, that

$$x\psi_{n'k'}(x) = -\mathrm{i}\,\partial_{k'}\psi_{n'k'}(x) + \mathrm{i}\,\mathrm{e}^{\mathrm{i}k'x}\partial_{k'}u_{n'k'}(x), \tag{52}$$

according to (36), (37*b*) and (39). One then obtains

$$\langle nk|x|n'k'\rangle = -\mathrm{i}\delta_{nn'}\partial_{k'}\delta_{k,k'} + \mathrm{i}\int_0^{Na} \mathrm{e}^{-\mathrm{i}(k-k')x} u^*_{nk}(x)\partial_{k'}u_{n'k'}(x)\,\mathrm{d}x. \tag{53}$$

Then, according to [5], the second term in (53) equals $N\delta_{k,k'}(u_{nk}|\mathrm{i}\,\partial_k u_{n'k})$ and thus, evaluating (53) for $k' = k$ and comparing it with (51), one concludes that expression (50) gives $\sigma_{nn'}(k) = 0$. However, as we pointed out earlier in connection with equation (42), $\partial_{k'}u_{n'k'}(x)$ is *not* periodic in x with period a and the claimed reduction of the second term in (53) is not correct, and the argument of [5] that $\sigma_{nn'}(k) = 0$ is invalid.

It is worth noting that the work of [5] has been criticised by others [1] as well. It was stated [1] that the error made in [5] lies in equation (40), which is used in [5] for the evaluation of $\delta_{nn'}\partial_{k'}\delta_{k,k'}$ for $k' = k$. It is asserted in [1] that equation (40) is incorrect. We believe that this remark is erroneous, since equation (40) is perfectly valid for a finite crystal, as was shown above. The Wannier functions centered near the edge of the system *are* orthogonal to the bulk Wannier functions, because they are periodic functions of x with period Na.

Most recently, after this study had been completed, the work of [5] was criticized in a comment [11], by pointing to a paradox that the work of [5], if correct, would result in. It was demonstrated there that the stair-function $S(x)$ must have non-vanishing interband matrix elements. The demonstration was based on the direct evaluation of $\langle nk|S|n'k'\rangle$ given by the second expression in (33) for a finite crystal. In our work, as in all other works under criticism here, we have considered the equivalent expression for $\langle nk|S|n'k'\rangle$ obtained by 'an integration by parts', namely the second expression in (43) and the last expression in (7), for a finite and an infinite crystal, respectively. This has allowed us to pinpoint precisely the flaws in the earlier studies, and at the same time give explicit expressions for the interband elements.

The study of the time-dependent problem in [4] is also in error, as it is based on the work reported in [5], which has just been shown to be invalid.

In a very recent publication [2] a yet different argument was presented carefully for a finite crystal, which claimed to show *indirectly* that $\sigma_{nn'}(k) = 0$ for the bands determined by the sawtooth-function of the electric field potential. We have, however, shown elsewhere [20] that the argument is in error for reasons similar to the ones associated with (50)–(53).

An argument based on the kq-representation has also been reported [3] to show that an electric field potential has no interband matrix elements for the bands determined by the periodic sawtooth-function of the potential, i.e. $\sigma_{nn'}(k) = 0$ for such bands. This argument [3], is, however, again wrong. In order to obtain the secular equation (20) in ref. [3], which demonstrates this claim, the author [3] must use an orthonormality relation for the Wannier functions namely

$$\int_0^a \mathrm{d}q\, w_n^*(q - ar) w_{n'}(q - ar') \propto \delta_{nn'}\delta_{rr'}. \tag{54}$$

This, however, is not valid, as only equation (40) is correct for the Wannier functions for the case of a finite crystal under consideration. In fact, if one tries to solve the Schrödinger equation for an electron in a periodic potential $V(x)$ and an electric field E in the kq-representation [3], namely

$$[-(1/2m)\partial^2/\partial q^2 + V(q) + eEq + eE\,\mathrm{i}\,\partial/\partial k]C(k, q) = \varepsilon C(k, q) \tag{55}$$

by expanding

$$C(k, q) = \sum_n A_{nk}\varphi_{nk}(q)$$

in terms of the electric-field-dependent Bloch functions $\varphi_{nk}(q)$ determined by

$$[-(1/2m)\partial^2/\partial q^2 + V(q) + eEq]\varphi_{nk}(q) = \varepsilon_{nk}\varphi_{nk}(q) \tag{56}$$

and the appropriate boundary conditions for $0 < q < a$, one finds easily

$$\varepsilon_{nk}A_{nk} + \mathrm{i}\,eE\frac{\partial}{\partial k}A_{nk} + eE\left(\frac{2\pi}{a}\right)\sum_{n'} A_{n'k}\left(\varphi_{nk}\left|\mathrm{i}\frac{\partial}{\partial k}\varphi_{n'k}\right.\right) = \varepsilon A_{nk} \tag{57}$$

with

$$\left(\varphi_{nk}\left|\mathrm{i}\frac{\partial}{\partial k}\varphi_{n'k}\right.\right) = \int_0^a \mathrm{d}q\,\varphi_{nk}^*(q)\,\mathrm{i}\frac{\partial}{\partial k}\varphi_{n'k}(q) \tag{58}$$

for the infinite crystal. For the finite crystal one replaces $\partial/\partial k$ by ∂_k, as defined before, and the normalization factor $(2\pi/a)$ by N. Thus, the interband matrix element in (57), which must be those of the stair-function potential, since the periodic sawtooth-function potential has been taken into account, are indeed identical to (8a) and (44), for the infinite and the finite crystal, respectively.

We comment now on an argument that is reported [1] to show that for the case of two (n, n') bands $\sigma_{nn'}(k) \neq 0$ quite generally. It is argued [1] that, since $(\psi_{nk}|\psi_{n'k}) \propto \delta_{nn'}$, ψ_{nk} and $\psi_{n'k}$ can be viewed as two perpendicular vectors in a two-dimensional space lying on a unit circle, and thus $(\partial_k\psi_{n'k})$ must be parallel to (ψ_{nk}), i.e. $\sigma_{nn'}(k) \propto (\psi_{nk}|\partial_k\psi_{n'k}) \neq 0$. However, we believe this argument is not complete, since the only conclusion we may draw from $(\psi_{nk}|\psi_{n'k}) \propto \delta_{nn'}$ is that $(\partial_k\psi_{nk}|\psi_{n'k}) + (\psi_{nk}|\partial_k\psi_{n'k}) = 0$, which does not entail the reported conclusion.

Finally, it is tempting to consider a different argument that seems to show that $\sigma_{nn'}(k) = 0$ quite generally. For the case of the infinite crystal, we propose to evaluate the matrix elements of the commutator $[H(k), x]$ in (14), not by integration by parts as

we did before, but by inserting a complete set of states between $H(k)$ and x. Since we are restricted to the unit cell $(0, a)$ we may take as usual for functions within $(0, a)$

$$(2\pi/a)\sum_n u_{nk}(x)u^*_{nk}(x') = \delta(x - x') \tag{59}$$

and find from (14), (10), (9*b*) and (5)

$$(1/m)(p_{nn'}(k) + k\delta_{nn'}) = \mathrm{i}(\varepsilon_{nk} - \varepsilon_{n'k})x_{nn'}(k) \tag{60}$$

in contradiction to (15). Comparing now (12) and (60) we find that $X_{nn'}(x) = x_{nn'}(k)$ for $n \neq n'$ and thus from (8*b*) we have in general $\sigma_{nn'}(k) = 0$. But clearly this procedure is wrong; the set $\{u_{nk}(x)\}$ for all n is not a complete set for the function x within $(0, a)$. If it was and (60) was correct, it would follow from (60) that $(p_{nn}(k) + k)/m = 0$, whereas from (11) with $n' = n$ we get by differentiation with respect to k the well-known relation

$$(2\pi/a)(u_{nk}|\partial H(k)/\partial k|u_{nk}) = (p_{nn}(k) + k)/m = \partial\varepsilon_{nk}/\partial k. \tag{61}$$

In fact, we can prove that, if $\sigma_{nn'}(k) = 0$ for $n' \neq n$ and we may use the completeness relation (59), then

$$\begin{aligned} m\,\partial^2\varepsilon_{nk}|\partial k^2 &= 1 + (2\pi/a)[(\partial u_{nk}/\partial k|p|u_{nk}) + (u_{nk}|p|\partial u_{nk}/\partial k)] \\ &= 1 + \sum_{n'\neq n}(p_{nn'}(k)x_{n'n}(k) - x_{nn'}(k)p_{n'n}(k)) \\ &= 1 + (1/\mathrm{i})(2\pi/a)(u_{nk}|[p, x]|u_{nk}) = 0 \end{aligned} \tag{62}$$

an obvious contraciction to the statement that $\sigma_{nn'}(k) = 0$ quite generally.

In view of these findings, it is clear that the calculation of the Zener tunnelling should not be based on the splitting of the electric field potential eEx into the sawtooth-function and the stair-function parts, since both have interband matrix elements. It is instead advantageous to base such a calculation on the interband elements $X_{nn'}(k)$, given in (48) and (9*a*), as indeed has been done in [14] and [15]. However, in these theories there are unsatisfactory features. For example, the interband elements are treated by perturbation theory, and the Zener current is calculated in the quasi-classical approximation. In addition the effects of collisions have not been considered. It is of basic interest to examine whether or under what conditions the $X_{nn'}$ can be treated as small, and how the Stark ladders, sharply defined when $X_{nn'}$ are neglected, are modified by their presence and how they affect the Zener current. We hope to address these points elsewhere.

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