Tightly Bound Electrons in a Uniform Electric Field

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The energy spectrum of tightly bound electrons in a uniform electric field is studied for finite systems. It forms the Stark ladder for almost all states except those near the band edges (these can be understood as surface states) and in the case of extremely low fields such that the potential drop across the entire sample is of the order of the bandwidth. This fact is independent of the boundary conditions. A two-band tight-binding model is solved, taking into account the interband coupling, and it is found that the spectrum is that of two interspaced Stark ladders. The experimental situation is briefly reviewed and the limitations and feasibility of observing Stark ladders in solids is discussed.

I. INTRODUCTION

The character of the energy spectrum of Bloch electrons in the presence of external electric or (and) magnetic fields has been extensively discussed in the literature.[1] A satisfactory understanding, however, has not yet been obtained even for the systems where the mutual Coulomb interactions can be neglected. In recent years there has been particular interest in the influence of an electric field on the energy spectrum.

Soon after the investigations by Slater[2] on the effects of the aperiodic perturbations on Bloch electrons, James[3] examined the electrons in a uniform electric field and suggested the possible quantization of the energy spectrum along the direction of the field. Katsura, Hatta, and Morita[4] examined the case of the tightly bound electrons within the one-band approximation. By finding exact solutions of a finite-difference Schrödinger equation, they found a discrete spectrum of equidistant levels. In retrospect this level quantization is identified with the Stark ladder (SL) to be discussed below. They also found that near the center of the band the energy spectrum of the finite crystal was nearly equal to that of the infinite crystal for the boundary condition that the wave function vanishes at the end of the crystal. Subsequently, Feuer[5] studied a two-band model of tightly bound electrons. A finite-difference Schrödinger equation was also encountered here and it was found that the uncoupled bands each gave rise to a SL. Solutions were obtained in which the interband dipole matrix element was treated as a perturbation and the otherwise interspaced SL's were taken to exactly coincide. Zener breakdown[6] was studied from this approach and the resulting tunneling probability was in qualitative agreement with that of Zener; the latter was obtained by a quite different method. A more general derivation of a SL was given by Kane[7] when he discussed the Zener tunneling in semiconductors. Solving Schrödinger's equation in momentum space within the one-band approximation he showed the existence of a SL with much simplicity. This quantization of the energy spectrum was extensively discussed by Wannier[8] who showed that if a solution of the one-electron Schrödinger equation in a periodic crystal potential and uniform electric field exists for some energy E, then the wave function $\psi_E(\vec{r})$ satisfies

$$\psi_E(\vec{r}) = \psi_{E-ebE_0}(\vec{r}+\vec{b}) \text{ (Wannier's theorem).} \quad (1.1)$$

Here E_0 is the electric field, $-e$ is the electronic charge, and $\vec{b}$ is a vector representing a period of the periodic crystal potential in the direction of the field and b is its length. If E is unique then it follows that a unique SL exists. In Eq. (1.1) it is essential that the system is infinitely large. Wannier[8] also presented detailed arguments for the existence of SL in terms of perturbative treatments of the electric field. Subsequently the effects of a magnetic field on tunneling process was treated by Argyres[9] and the optical absorption was examined by Callaway.[10] Both are based on the wave function that Kane obtained. After these pioneering works, various investigators[11,12] examined the problem in a somewhat similar fashion.

Zak,[13] on the other hand, has put forward various arguments which call the existence of a SL into question. He first claimed that there is a mathematical inconsistency in the usual derivation of a SL if one makes the following assumptions at the same time: (a) periodic boundary condition, (b) one-band approximation, and (c) macroscopically large system such that the momentum variable can be treated as a continuous variable. Later he pointed out that E in Eq. (1.1) is not uniquely determined and might be arbitrary, resulting in a continuous spectrum. Zak furthermore argued that the energy spectrum should be sensitive to the imposed boundary conditions. Rabinovitch and Zak[14] in particular found a discrete energy spectrum dif-

ferent from a SL for both free electrons and Bloch electrons. In the latter case they introduced a sinusoidal potential and treated the spectrum numerically for a finite system under the rigid-wall boundary condition. Recently the problem of boundary conditions has been discussed by Shockley[15] who claimed that almost all physically relevant states will form a SL with minor modifications irrespective of the boundary. Apart from those rather formal questions, there has been a naive concern about the compatibility of a SL with the Bloch band in the low-field limit.

On the experimental side, tunneling[16] and optical[17] studies aimed at verifying the existence of the SL have been inconclusive and also questioned. However, recent measurements of the nonlinear conductivity by Maekawa[18] are worth noticing. We discuss this in Sec. IV. Other recent experimental support for the existence of the SL has been given in the optical absorption study of Koss and Lambert, [19] although, as these authors pointed out, the experimental uncertainty is rather large.

In this paper we first study a one-band model within the tight-binding approximation where the system is put at an arbitrary size and the boundary conditions are either periodic or rigid walls at both ends. Thus we remove two of the above-mentioned restrictions, (a) and (c).

Although, as is well known, the single-band model leads to a unique SL in a one-dimensional system, this is almost certainly not true for the full multiband system. It is reasonable to expect that the energy spectrum will in general[20] be continuous as Zak[13] and others[21] pointed out. (We note that this possibility is consistent with Wannier's theorem since the theorem also applies to the empty lattice.) However, we argue that this situation would not preclude observation of the SL quantization associated with a given band. We have also solved a two-band tight-binding model and found the spectrum to be comprised of two interspaced SL. We have used this solution in presenting our argument for the observation of a single-band SL.

II. BOUNDARY CONDITIONS IN A SINGLE BAND

We investigate one-dimensional Bloch electrons within the tight-binding approximation represented by the Hamiltonian

$$\mathcal{H} = \sum_{l,l'=1} t_{ll'} a_l^\dagger a_{l'} + w \sum_{l=1}^{N} l a_l^\dagger a_l \,, \tag{2.1}$$

where $a_l^\dagger(a_l)$ is the creation (annihilation) operator at the lth Wannier site. The transfer energy $t_{ll'}$ is assumed to be finite for nearest-neighbor hopping only, $t_{ll'} = -t(t>0)$, and $w = eE_0 a$, where $-e$, E_0, and a are the electronic charge, the external electric fields, and the lattice spacing, respectively. In this section we have neglected interband matrix elements of the coordinate operator. Although Eq. (2.1) is one dimensional, extensions to a three-dimensional tight-binding model is straightforward provided the electric field is in the direction of a crystal axis. The present model has been employed extensively in various studies. However, all of the previous investigations were concerned with macroscopically large systems. In the following we examine the effects of both finiteness of the crystal and boundary conditions in detail. Equation (2.1) also enables us to discuss both the limit of localized atomic electrons ($t=0$), where the SL is obviously present, and the limit of free electrons discussed by Rabinovitch and Zak[14] ($wt^{-1} \to 0$ retaining $a^2 t$ finite).

The various physical regimes are characterized by two dimensionless parameters $\alpha = t/w$ and $\bar{\alpha} = t/Nw$, where N is the total number of lattice sites and $w = eE_0 a$. The parameter α describes the degree of localization of a wave packet around an atomic site, since t and w represent the kinetic energy associated with the hopping and the potential difference between neighboring sites, respectively. The auxiliary parameter $\bar{\alpha}$ characterizes the competition between the kinetic energy and the potential drop due to the electric field across the system. For $\bar{\alpha} \ll 1$ the energy spectrum is shown to be insensitive to the boundary conditions and forms a SL except for levels near the edge of the band, where we find derivations from the SL for $\alpha > 1$. The fraction of levels deviating from the SL, however, is vanishingly small in the limit of large N. In this sense almost all states form a SL. For $\bar{\alpha} \geq 1$ the SL disappears and the levels approach the free Bloch spectrum and are sensitive to the boundary conditions.

In order to solve the eigenvalue equation $\mathcal{H}\Phi = E\Phi$ for the Hamiltonian in Eq. (2.1), we expand Φ in terms of localized Wannier states

$$\Phi = \sum_{l=1}^{N} c_l a_l^\dagger |0\rangle \,,$$

where $|0\rangle$ is the vacuum. We obtain the following secular equation for the expansion coefficient c_l:

$$(\epsilon\alpha - l)c_l = \alpha(c_{l+1} + c_{l-1}) \,. \tag{2.2}$$

Here $\epsilon = E/t$ and $\alpha = t/w$. Exact solutions to Eq. (2.2) were first given in Refs. 4 and 5. This type of equation was also treated by one of the present authors[22] in connection with the magnon bound-state spectrum in a magnetic salt. [23] By noting that Eq. (2.2) has the same form as the recursion formula $Z_{\nu+1}(x) + Z_{\nu-1}(x) = (2\nu/x) Z_\nu(x)$ for the solutions $Z_\nu(x)$ to the Bessel equation, [24] we can immediately write the general solution of Eq. (2.2) in the form

$$c_l = A J_{l-\epsilon\alpha}(2\alpha) + B Y_{l-\epsilon\alpha}(2\alpha) \,, \tag{2.3}$$

where J_ν and Y_ν are the usual Bessel and Neuman

functions, $\sin\nu\pi Y_\nu(x) = \cos\nu\pi J_\nu(x) - J_{-\nu}(x)$. The arbitrary real constants A and B are determined by means of the boundary conditions. For convenience we have chosen the real solutions to Eq. (2.2), thereby excluding current-carrying states. (Current-carrying states can be discussed in terms of the complex Hankel functions.[24])

A. Rigid-Walls Boundary Condition

By imposing rigid walls at both ends of the crystal, we arrive at the boundary conditions $c_0 = c_{N+1} = 0$ which lead to the eigenvalue equation

$$J_{-\epsilon\alpha}(2\alpha)Y_{N+1-\epsilon\alpha}(2\alpha) - J_{N+1-\epsilon\alpha}(2\alpha)Y_{-\epsilon\alpha}(2\alpha) = 0 \ . \quad (2.4)$$

In the *high*-field limit, $\alpha \ll 1$ (i.e., $w \gg t$), the left-hand side of Eq. (2.2) dominates and we get $\epsilon\alpha = n (n = 1, \ldots, N)$, which is the SL. This is the limit of atomic electrons localized at each Wannier site. A more careful analysis based on Eq. (2.4) by means of the power series expansions of the Bessel and Neuman functions yields (keeping only the leading term)

$$\alpha^{-(N+1)}[\Gamma(1-\epsilon\alpha)\Gamma(\epsilon\alpha - N)\sin(\epsilon\alpha - N)\pi]^{-1} \quad (2.5)$$

The poles of the Γ function imply $\epsilon\alpha = n$, i.e., the SL.

Let us next consider the spectrum at *intermediate* and *low* fields, i.e., $\alpha \approx 0(1)$ but $\bar{\alpha} \ll 1$. We first demonstrate the existence of a SL for almost all states in a macroscopic system. For this purpose we distinguish between states which are close to either band edge, i.e., $\epsilon\alpha \approx 0(1)$ or $N - \epsilon\alpha \approx 0(1)$, and the remaining states which occupy the bulk of the spectrum. In the latter case we make use of the asymptotic expressions for the Bessel and Neuman functions for large order and fixed argument

$$\begin{aligned} J_\nu(x) &\xrightarrow{\nu\to\infty} (2\pi\nu)^{-1/2}(ex/2\nu)^\nu \ , \\ Y_\nu(x) &\xrightarrow{\nu\to\infty} (2/\pi\nu)^{1/2}(ex/2\nu)^{-\nu} \ , \end{aligned} \quad (2.6)$$

and obtain the eigenvalue equation, $\tan[\epsilon\alpha\pi] = 0$, which implies $\epsilon\alpha = n$ (integer), i.e., a SL. The fraction of states near the band edges, which show deviations from a SL, is of order N^{-1} and therefore vanishingly small for a macroscopic system.[25] The above arguments demonstrate the existence of a SL for almost all states even in the presence of rigid-wall boundary conditions.

In order to investigate the energy spectrum near the lower band edge, we assume without loss of generality that $N \to \infty$, in which case Eq. (2.4) reduces to

$$J_{-\epsilon\alpha}(2\alpha) = 0 \ . \quad (2.7)$$

In the high-field limit, Eq. (2.7) yields a SL as discussed above. At low fields, $\alpha^{-1} \ll 1$, we make use of the following double asymptotic expansion of the Bessel function:

$$J_{2\alpha\cos\theta}(2\alpha) \xrightarrow{\alpha\to\infty} \cos[2\alpha(\sin\theta - \theta\cos\theta) - \tfrac{1}{4}\pi] \ . \quad (2.8)$$

The energy spectrum $\epsilon = -2\cos\theta$ is given by the zeros of Eq. (2.8), i.e., $\sin\theta - \theta\cos\theta = \pi(n + \frac{3}{4})/2\alpha$ (n positive integer). By expanding near the lower band edge $\epsilon = -2$, we obtain the spectrum

$$\epsilon_n = -2 + \alpha^{-2/3}[3\pi(n+\tfrac{3}{4})/2]^{2/3} \ . \quad (2.9)$$

The expression (2.9) is of the same form as the energy spectrum obtained by Rabinovitch and Zak[14] for free electrons in an electric field if we replace $(2a^2t)^{-1}$ by an effective mass m. We redefine the energy origin at the lower edge of the band and restore the proper energy units, we have

$$\epsilon_n = [3\pi eE_0(n+\tfrac{3}{4})/2(2m)]^{1/2} \quad (2.10)$$

The spectrum of Eq. (2.10) represents the surface states at one (lower-electric-field potential) side of the crystal. In the case of finite bandwidth, however, the spectrum continuously changes to a SL around n_0th eigenstate which satisfies $\epsilon_{n_0} \approx 2$, or

$$n_0 \approx (16\alpha/3\pi - \tfrac{3}{4}) \ . \quad (2.11)$$

In the *extreme* low-field limit, where $\bar{\alpha} \gg 1$, we obtain the energy spectrum of free Bloch electrons $\epsilon_n = -2\cos(\pi n/N)$, $n = 0, 1, \ldots, N-1$. This can be shown using Eq. (2.4) by expanding the asymptotic expression (2.8) and the corresponding one for Y_ν in orders of $N\alpha^{-1}$ for $N\alpha^{-1} \ll 1$. Thus the spectrum changes continuously in the extreme low-field limit for finite N. For an infinite system the zero-field limit is singular as shown by Eq. (2.10).

The right-hand side of Fig. 1 illustrates the field dependence of the energy spectrum for rigid-wall boundary conditions. For simplicity we have set $N = 50$ in the plot. We stress that for large N almost all eigenvalues form a SL. A more quantitative plot of the field dependence of the lowest few levels for $\alpha^{-1} \lesssim 1$ can be found in Fig. 1 of Ref. 22.[26]

B. Periodic Boundary Condition

In this case, the eigenvalue equation is given by

$$\frac{Y_{l-\epsilon\alpha}(2\alpha) - Y_{l+N-\epsilon\alpha}(2\alpha)}{J_{l-\epsilon\alpha}(2\alpha) - J_{l+N-\epsilon\alpha}(2\alpha)} = \text{constant independent of } l \ . \quad (2.12)$$

The energy spectrum determined by this condition is almost identical to that of the rigid-walls boundary condition except at extremely low values of the field, i.e., $\bar{\alpha} > 1$. This is related to the fact that the zero-field Bloch spectrum, $\epsilon_n = -2\cos(2\pi n/N)$ ($n = 0, 1, \ldots, N-1$), is doubly degenerate except for the lowest state. The degeneracy is lifted by the electric field and for $\bar{\alpha} < 1$ the spectrum becomes insensitive to the boundary conditions. The eigenvalue spectrum in the case of periodic boundary conditions is plotted on the left-hand side of Fig. 1. Thus we have confirmed the existence of a SL for

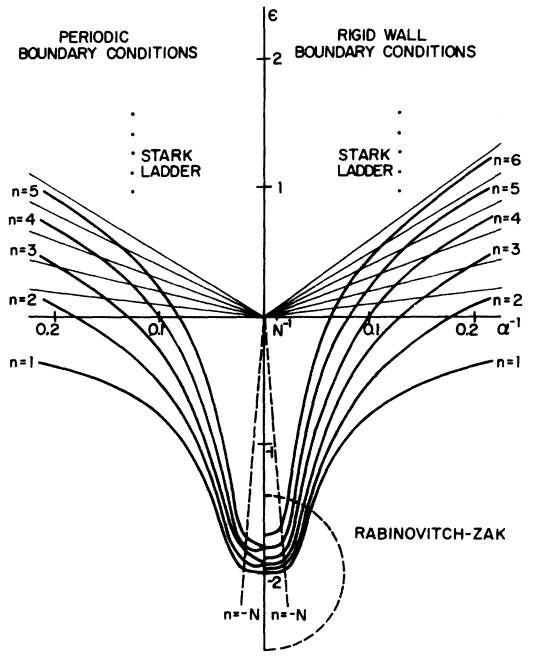

FIG. 1. A schematic representation of the electric field dependence of the energy spectrum ϵ in the case of rigid-wall boundary conditions (right-hand side of energy axis) and in the case of periodic boundary conditions (left-hand side of energy axis). For $\alpha^{-1}=eE_0a/t$ less than N^{-1} (N is the total number of lattice sites) the spectrum is essentially that of free Bloch electrons and is sensitive to the boundary conditions. For higher fields $\alpha^{-1}\gg N^{-1}$ the spectrum forms a Stark ladder in almost the whole energy region. Deviations from the Stark ladder is appreciable only for states near the edge of the band and for weak fields $\alpha\sim 1$.

a finite one-dimensional tight-binding band.

C. Infinite Crystals

As we have seen, if the crystal is large the boundary conditions have no effects on the energy spectrum for almost all states except those very near the surfaces. This is in accord with Shockley's observation.[15] The fact that the present model yields a SL in infinite crystals is also simply seen[4,5] from the requirement of the normalizability of the wave function C_l, Eq. (2.3). By the redefinition of the origin of the coordinate at the center of the crystal, this condition is written as

$$\sum_{l=-\infty}^{\infty} |C_l|^2 < \infty , \tag{2.13}$$

which is satisfied only for $C_l = J_{l-n}(2\alpha) \equiv C_l^{(n)}$, where n is an arbitrary integer related to the energy eigenvalue $\epsilon_n = nw$. The completeness and orthogonality for these wave functions follow from

$$\sum_{l=-\infty}^{\infty} J_{n+l}(2\alpha)J_{n'+l}(2\alpha) = \delta_{n,n'} . \tag{2.14}$$

Thus by use of the one-particle operator

$$\alpha_n = \sum_{l=-\infty}^{\infty} J_{l-n}(2\alpha)a_l , \tag{2.15}$$

the Hamiltonian, Eq. (2.1), is diagonalized as

$$\mathcal{H} = \sum_{n=-\infty}^{\infty} \epsilon_n \alpha_n^\dagger \alpha_n . \tag{2.16}$$

Here α_n and a_l refer to destruction operators for an electron on the nth rung of the SL and the lth Wannier site, respectively. Note that the wave packet corresponding to the nth rung of the SL has a center at R_n and its width is of the order of αa. Correspondingly, the one-particle propagator defined by

$$K(R_r, R_s, \tau) \equiv \langle 0 | a_r(\tau) a_s^\dagger(0) | 0 \rangle \tag{2.17}$$

can be written in a closed form as

$$\begin{aligned} K(R_r, R_s, \tau) &= \sum_{l=\infty}^{\infty} J_{r-l}(2\alpha) J_{s-l}(2\alpha) e^{ilw\tau} \\ &= e^{irw\tau} e^{-i(r-s)(w\tau-\pi)/2} \\ &\quad \times J_{r-s}(4t(\sin\tfrac{1}{2}w\tau)/w) . \end{aligned} \tag{2.18}$$

If we define $K(k, \tau)$ by

$$K(k, \tau) \equiv 1/N \sum_{r,s} e^{ik(R_r - R_s)} K(R_r, R_s, \tau),$$

we obtain

$$\lim_{E_0 \to 0} K(k, \tau) = e^{i2t\tau \cos ka} , \tag{2.19}$$

which is the correct propagator in the absence of the electric field. Thus although the energy spectrum is discontinuous at $E_0 = 0$, this one-particle propagator goes correctly to the one in zero field (since the wave functions at energies outside the zero-field bandwidth interfere destructively as that limit is approached), implying that other physical observables will behave accordingly.

Wannier's theorem, Eq. (1.1), applies to an infinite crystal of the present model, Eq. (2.1), and therefore does not say anything about finite crystals. In the following we wish to show how, working with an infinite crystal, a boundary condition that has a sensible interpretation can be imposed.

In Eq. (2.16), for large negative n, states of arbitrarily large negative energy occur in the spectrum. These states appear because electrons can move to infinity in the negative x direction in the model and, therefore, find themselves in a region of arbitrarily large negative potential energy. Real solids are bounded, of course, and the surface of the solid presents a barrier which prevents this from occurring. In order to simulate the surface of a solid, let us try an approach taken from other situations in which infinitely negative-energy fermion states have appeared,[27] and fill up all the states up to some energy. Without loss of general-

ity, we take this energy to be zero. Because of the relationship, Eq. (2.15), between n and R_l in the wave function, filling the states up to some energy is essentially equivalent to filling the infinite solid on one side of a certain position. Thus, owing to the exclusion principle, rather than a physical barrier, additional electrons do not move to regions of large negative energy, but remain in the region spanned by the positive rungs of the SL.

Since we have the exact wave functions for the states, we can make these statements mathematically precise. The probability that the site at R_l is filled, if we fill the states referring to n from $-\infty$ to 0, is given by

$$\rho(R_l)=\sum_{n=-\infty} J_{n-l}^2(2\alpha)\ ; \tag{2.20}$$

$\rho(R_l)$ is a monotonic function which satisfies the equations

$$\lim_{R_l\to-\infty}\rho(R_l)=1\ , \tag{2.21}$$

$$\lim_{R_l\to\infty}\rho(R_l)=0\ . \tag{2.22}$$

Furthermore,

$$\rho(-R_l)=\rho(0)+\sum_{\lambda=1} J_\lambda^2(2\alpha) \tag{2.23}$$

and

$$\rho(R_l)=\rho(0)-\sum_{\lambda=1}^{l} J_{\lambda-1}^2(2\alpha) \tag{2.24}$$

for $l>0$. Here

$$\rho(0)=\tfrac{1}{2}[1+J_0^2(2\alpha)]\ . \tag{2.25}$$

Simple numerical analysis shows that this function, $\rho(R_l)$, varies from 0.01 to 0.99 in a region of width L, where

$$L=2\alpha a=4t/eE_0\ . \tag{2.26}$$

Thus, the thickness of the barrier we simulate by filling the negative-energy states is field dependent and the stronger the field, the more abrupt the barrier.

III. TWO-BAND MODEL IN INFINITE CRYSTALS

The effects of interband coupling were already discussed by Feuer[5] who restricted the strength of the electric field to the specific values that yielded two coinciding SL's in the absence of interband coupling. In this section we discuss this problem more generally based on the Hamiltonian for tightly bound electrons,

$$\begin{aligned}\mathcal{H}=&-\Delta\sum_{l=-\infty}^{\infty} a_l^\dagger a_l + t\sum_{l=-\infty}^{\infty}(a_l^\dagger a_{l+1}+a_{l+1}^\dagger a_l)+\Delta\sum_{l=-\infty}^{\infty} b_l^\dagger b_l + t'\sum_{l=-\infty}^{\infty}(b_l^\dagger b_{l+1}+b_{l+1}^\dagger b_l)\\ &+w\sum_{l=-\infty}^{\infty} l(a_l^\dagger a_l+b_l^\dagger b_l)+V\sum_{l=-\infty}^{\infty}(a_l^\dagger b_l+b_l^\dagger a_l)\ .\end{aligned} \tag{3.1}$$

Here a_l (b_l) is the destruction operator referring to the lower (upper) band. The first four terms represent the two Bloch bands which have the half-bandwidths $2t$ and $2t'$, respectively. We chose the energy origin such that the centers of gravity of the two bands are symmetrically displaced about it and separated by 2Δ. The tight-binding approximation requires $2\Delta\gg 2|t|$ and $2\Delta\gg 2|t'|$. The last two terms are due to the electric field. We have $V=eE_0X$, where X is the dipole matrix element between two atomic states at the same site. We have neglected the matrix elements of electric field between neighboring sites. By introducing

$$\begin{aligned}\alpha_n&=\sum_{l=-\infty}^{\infty} J_{l-n}(2\alpha)a_l\ ,\\ \beta_n&=\sum_{l=-\infty}^{\infty} J_{l-n}(2\alpha')b_l\ ,\end{aligned} \tag{3.2}$$

with $\alpha=t/eaE_0$ and $\alpha'=t'/eaE_0$, we rewrite Eq. (3.1) as

$$\begin{aligned}\mathcal{H}=&\sum_{n=-\infty}^{\infty}(\epsilon_n^-\alpha_n^\dagger\alpha_n+\epsilon_n^+\beta_n^\dagger\beta_n)+eE_0X\\ &\times\sum_{n,n'=-\infty}^{\infty} J_{n-n'}(2\alpha-2\alpha')(\alpha_n^\dagger\beta_{n'}+\beta_{n'}^\dagger\alpha_n)\ .\end{aligned} \tag{3.3}$$

Here, $\epsilon_n^\pm=\pm\Delta+neaE_0$ and we have used the identity

$$\sum_{l=-\infty}^{\infty} J_{n-l}(2\alpha)J_{n'-l}(2\alpha')=J_{n-n'}(2\alpha-2\alpha')\ . \tag{3.4}$$

Eigenvalue equations for Eq. (3.3) are cast into the form

$$\begin{aligned}(\omega-\epsilon_n^-)\alpha_n&=V\sum_{n'=-\infty}^{\infty} J_{n-n'}(2\alpha-2\alpha')\beta_{n'}\ ,\\ (\omega-\epsilon_n^+)\beta_n&=V\sum_{n'=-\infty}^{\infty} J_{n-n'}(2\alpha'-2\alpha)\alpha_{n'}\ .\end{aligned} \tag{3.5}$$

It is seen that, through the interband matrix elements of the electric field, the nth rung of either ladder is coupled to all of the rungs of the other ladder. The energy spectrum of this coupled set of difference equations is found to be comprised of two interspaced Stark ladders (see Appendix). In the special case that $t=t'$ or $\alpha=\alpha'$, which implies an indirect band gap, the Hamiltonian Eq. (3.3) becomes

$$\mathcal{H} = \sum_{n=-\infty}^{\infty} [\epsilon_n^- \alpha_n^\dagger \alpha_n + \epsilon_n^+ \beta_n^\dagger \beta_n + V(\alpha_n^\dagger \beta_n + \beta_n^\dagger \alpha_n)] \quad (3.6)$$

The eigenvalues ω_n are simply given by

$$\omega_n^\pm = \pm (\Delta^2 + V^2)^{1/2} + neaE \ . \quad (3.7)$$

The spectrum is that of two interspaced SL's, and the energy spectrum of the system as a whole is no longer that of a simple SL. Thus it generally happens that the nth state belonging to one rung, for example ω_n^+ of Eq. (3.7), has an energy eigenvalue close to the n'th of the other rung $\omega_{n'}^-$; or

$$|\omega_n^+ - \omega_{n'}^-| = |2(\Delta^2 + V^2)^{1/2} + (n - n')eaE_0| \ll eaE_0 \ . \quad (3.8)$$

However, the coupling between these two states is very small if

$$(\Delta^2 + V^2) \gg t \quad (3.9)$$

is satisfied. This comes from the fact that the centers of the wave packets are apart, by Eq. (3.8), as much as

$$|(n - n')a| \approx 2(\Delta^2 + V^2)^{1/2}/eE_0 \quad (3.10)$$

and the spread of each of the packets is of the order $\alpha a = 2t/eE_0$. Thus two wave packets do not overlap and would have little coupling under the condition of Eq. (3.9). In such a case, certain physical properties related to spatially local probes would behave as if there is only one SL. If Eq. (3.9) is not satisfied, states belonging to different rungs couple appreciably through such local perturbations.

IV. DISCUSSION

We summarize our results as follows: (i) In a macroscopically large system we confirm the existence of a Stark ladder in a one-band model with either of the periodic boundary condition or the rigid-walls boundary condition. (ii) In a finite system the energy spectrum does not yield a SL in a rigorous sense, but the deviations from a simple SL are very small except in two cases. One is the case of extremely low fields where the potential difference between two surfaces due to an electric field is comparable to the bandwidth and the other is the case of states near the band edges (surface states) in arbitrary fields. In the case of an infinite bandwidth (an effective mass region), all of the states are under the influence of rigid walls and then it is natural that the spectrum Rabinovitch and Zak[14] found for this case is different from the simple SL. (iii) In a model of a two-band system, the energy eigenvalue no longer forms a SL but yields two interspaced SL's. However, if the band gap is larger than the bandwidth, nearby energy states associated with different ladders will be spatially separated and it is meaningful to discuss a single SL over a given spatial region.

Although our studies have been for one-dimensional models of crystals, we note that the situation is somewhat different in a two- or three-dimensional system. We take the former case as an example, but the similar arguments apply to the latter. If the electric field lies in a *rational* direction in the sense that it is parallel to a vector $(m\vec{a}_1, n\vec{a}_2)$ where $\vec{a}_1$ and $\vec{a}_2$ are two fundamental lattice vectors and m and n are arbitrary integers, the electronic motion is periodic in both real and momentum spaces and the spectrum is discrete along the electric field. This can be easily deduced from the arguments of Kane.[7] [Note that $(k_2 - k_1)$ in Eq. (5) of Ref. 7 is the sum of the segments of the path in the first Brillouin zone.] The spectrum is continuous with respect to the motion perpendicular to the field. In this sense the whole energy spectrum consists of the continous and the discrete components in this case of the *rational* field direction. If the field lies in an *irrational* direction, the spectrum even in the direction of the field becomes continuous since the period of the motion becomes infinite, and the entire spectrum consists of two continuous components. This rationality of the electric field direction for the quantization of the spectrum might be compared with the rationality of the strength of the magnetic field encountered in the discussions of Brown,[28] Chambers,[29] and Zak.[30]

We again stress that these peculiar features of the eigenvalues will not prevent us from observing the simple structure of a Stark ladder, due to the fact that the coupling between these neighboring states is not always strong.

There have been no definite observations of the SL until the recent experiments by Maekawa[18] and Koss and Lambert.[19] Maekawa found a stepwise increase of the electrical conductivity in ZnS as a function of electric field. These results were theoretically analyzed by Saitoh[12] on the basis of Kane's function.[7] In this experiment a thin film with a thickness of the order of 1 μm was used and the applied electric field was $\sim 10^6$ V/cm. Since the bandwidth is nearly 3 eV,[31] we have $\alpha^{-1} = eEa/t \approx 2\times10^{-2}$ ($a = 3$ Å), which is nearly two orders of magnitude larger than $N^{-1} = a/(\text{film thickness}) \simeq 3\times10^{-4}$. In this sense the experiment is definitely in the region of the discrete spectrum except for the broadening of the states due to the motion perpendicular to the field. From Fig. 1, on the other hand, we note that in this case the spectrum deviates strongly from a SL near the band edges. These deviations will not be important, however, for the current-carrying electrons running from one side of the surface to the other, since the number of atoms which occupy surface

regions is $2n_0 \approx 4t/eEa \approx 200$ [Eq. (2.11)] and then electrons spend almost all of their time in the bulk region. Thus the analysis by Saitoh who treated the system as a bulk sample is justified in this respect. However, the condition, Eq. (3.9), for the validity of the one-band approximation is not satisfied so well since the band gap is ~4 eV and then SL of different rungs would couple to each other owing to such perturbations as electron phonon and impurity scatterings. Apart from this interband coupling, the present system has another complication owing to the three-dimensional character. Applications of the high magnetic fields in the same direction of the electric field might be of use since the motion perpendicular to the electric field can be quenched. We note, however, that more detailed investigations based on current-carrying solutions [complex solutions to Eq. (2.2)] are necessary for understanding such nonlinear transport phenomena.

Besides such irreversible processes, it would also be of interest to see the gradual change of the energy spectrum from the surface to the bulk region. Perhaps optical measurements will be useful in this regard. (We note the measurement by Koss and Lambert[19] in the bulk region.) Of course the purity and the thickness of samples are important factors in this kind of experiment. The former determines both the carrier number and the relaxation time and the role of the latter has been discussed in this paper. Apart from usual solid-state materials, the narrow-bandwidth organic solids[32] are of particular interest since they can be intrinsically one dimensional and the condition Eq. (3.9) for a one-band approximation is easily satisfied.

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APPENDIX

We shall demonstrate that the energy spectrum of Eq. (3.5) is comprised of two interspaced Stark ladders. We introduce Fourier transforms of α_n and β_n according to

$$a(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ink a} \alpha_n \,, \tag{A1}$$

$$b(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ink a} \beta_n \,. \tag{A2}$$

Note that $a(k + 2\pi/a) = a(k)$ and $b(k + 2\pi/a) = b(k)$. We substitute Eqs. (A1) and (A2) in Eq. (3.5) and easily obtain

$$\left(\omega + \Delta - ieE_0 \frac{d}{dk}\right) a(k) = Ve^{-2i(\alpha - \alpha')\sin ka} b(k) \,, \tag{A3}$$

$$\left(\omega - \Delta - ieE_0 \frac{d}{dk}\right) b(k) = Ve^{2i(\alpha - \alpha')\sin ka} a(k) \,. \tag{A4}$$

In obtaining the Fourier transform of the right-hand sides of Eqs. (A3) and (A4) we used the integral representation of the Bessel function,[24]

$$J_n(x) = (1/\pi) \int_0^\pi d\theta \, e^{i(n\theta - x \sin\theta)} \,.$$

If we define

$$a(k) = A(k) \, e^{-(i/eE_0)(\omega + \Delta)k}$$

and

$$b(k) = B(k) \, e^{-(i/eE_0)(\omega - \Delta)k} \,,$$

then, from Eqs. (A3) and (A4) we obtain

$$-ieE_0 \frac{d}{dk} A(k) = Ve^{iF(k)} B(k) \,, \tag{A5}$$

$$-ieE_0 \frac{d}{dk} B(k) = Ve^{-iF(k)} A(k) \,, \tag{A6}$$

where

$$F(k) = \frac{2\Delta}{eE_0} k - 2(\alpha - \alpha') \sin ka \,.$$

After differentiation of Eq. (A6) and combining with Eq. (A5) we obtain

$$\frac{d^2B}{dk^2} + \left(\frac{V}{eE}\right)^2 B - i\left(\frac{2\Delta}{eE} - 2(\alpha - \alpha')\cos ka\right) \frac{dB}{dk} = 0 \,. \tag{A7}$$

Since Floquet's theorem[33] applies to this differential equation, the solution must be of the form $B(k) = e^{i\lambda k} P(k)$, where $P(k + 2\pi/a) = P(k)$ and $\lambda = \lambda(V, \Delta, t - t')$. This implies that

$$b(k) = e^{i[\lambda - (\omega - \Delta)/eE]k} P(k) \,, \tag{A8}$$

but the periodicity condition on $b(k)$ requires that

$$\lambda - (\omega - \Delta)/eE = na \quad (n = \text{integer}) \,. \tag{A9}$$

This gives

$$\lambda_n = \Delta + neaE + eE\lambda \,, \tag{A10}$$

the familiar ladder spectrum. It is seen that the condition (A9) makes the function $a(k)$ also periodic in momentum space. By repeating arguments for $A(k)$ similar to those leading to Eq. (A7), we will get the spectrum (A10) with different λ.

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