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Electrons in Crystals in a Finite-Range Electric Field*

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The problem of an electron in a finite-range constant electric field is treated; energy levels and eigenfunctions are calculated for the "empty crystal" and for a Mathieu-type model crystal. It is shown that the addition of boundary conditions may change the solution drastically. The influence of different boundary conditions on the eigenvalues and eigenfunctions is discussed and it is found that the former are relatively insensitive while the latter are sensitive to a change in boundary conditions. The result for the eigenvalues is shown to be consistent with an extension of the Born-Ledderman theorem to electronic states in finite crystals. The effective-mass approximation is shown to hold for this model even for moderate fields and use is made of it to explain the complex behavior of the wave functions near the bands' edges. All in all, a clear detailed picture, although limited in scope, is presented of properties of electrons in crystals under the influence of external electric fields.

I. INTRODUCTION

For many years the fundamental problem of a crystal in an external electric field has attracted much attention.[1] Some features of the issue, e.g., the behavior of the optical absorption in the presence of the field,[1-8] are still in dispute. For this effect, instead of a sharp absorption edge above the frequency connected with the band gap in the absence of the field, one gets an "exponential tail" of absorption in longer wavelengths, or smaller energies (the Franz-Keldish effect). Superposed on this absorption curve is a structure hitherto explained to be due to a "Stark ladder" effect. But the existence of the Stark ladder[4,8] and the details of the Franz-Keldish[7] effect are subjects far from being agreed upon. Several pictures have been suggested to describe this problem, but all of them treat the infinite crystal case in an infinite-range electric field.

In this paper we show how the introduction of boundaries into the problem influences the results obtained, bearing in mind that in physical reality the crystal's range and the range of the electric field are finite. We limit ourselves to the case of zero current and we treat the one-dimensional case as it contains the essential physical problem.

In Sec. II we treat analytically the case of an empty lattice in an electric field with appropriate boundary conditions. The energy eigenvalues and the eigenfunctions are calculated. For high energies the solutions have the known correct simple potential-well behavior. The applicability of this model to the case of a crystal in an applied electric field is discussed.

However, to get a more accurate picture (including the periodic potential and its effect), we have treated a model—a one-dimensional Mathieu-type finite crystal in an electric field—which incorporates enough real crystal properties to give us a clear picture of the main features, albeit only numerically. Changes in the energy distribution and in the eigenfunctions in the presence of the field are covered in detail, as well as side issues dealing with the finiteness of the crystal and with the influence of the boundary conditions. In Sec. III the problem is stated and discussed, and the different types of boundary conditions with which we deal are compared, using an extension of the Born-Ledderman (BL) theorem (Appendix D). The picture of the behavior of the crystal in the presence of the field is clarified using the numerical results. The decrease of the forbidden gap between two energy bands is shown as a function of the field. No Stark ladder is obtained in the energy spectrum. The two limiting cases of zero field and a strong field are considered and are shown to agree with the expected results. Wave functions for several field values are compared. In Sec. IV it is shown that for this finite model the effective-mass approximation (EMA) is really a very good approximation even for relatively high fields.

II. EMPTY LATTICE

Let us begin by solving the case of a semifree electron in an electric field; i.e., we take a potential well to represent the crystal (Fig. 1). The important point is the finite range of this well. The

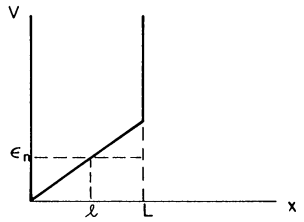

FIG. 1. Empty-lattice infinite-well potential in the presence of a finite-range electric field vs distance in the crystal. l is the distance where the energy level ϵ_n equals the potential (turning point).

time-independent Schrödinger equation for this problem is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + eEx\right)\Psi = \epsilon\Psi \ , \tag{2.1}$$

where e is the electron charge, ϵ is the energy eigenvalue, and E is the magnitude of the electric field.

For the infinite-range case, i.e., for the case where x is in the domain $(-\infty, +\infty)$, a solution to (2.1) was given[9] subject to the usual boundary conditions, namely, that the function not diverge for $\pm\infty$. The way to achieve this solution is to Fourier transform (2.1) and to obtain the solution in momentum space. The *one* solution then is the Airy function $\mathrm{Ai}(Z)$, where

$$Z = \alpha_1^{1/3}x - \tilde{\epsilon}/\alpha_1^{2/3} \ ; \quad \alpha_1 = 2meE/\hbar^2 \ ; \quad \tilde{\epsilon} = 2m\epsilon/\hbar^2 \ . \tag{2.2}$$

A solution exists for every value of the energy, from $\epsilon = -\infty$ to $\epsilon = +\infty$.

On the other hand, for the finite case, when the crystal goes, say, from 0 to L, the situation is completely different. The general solution of (2.1) can be given as a linear combination of *two* independent functions $\mathrm{Ai}(Z)$ and $\mathrm{Bi}(Z)$. The Bi solution cannot be discarded[10] for the finite case. Here the boundary conditions determine a discrete set of allowed energy levels with a lower bound, which can be taken as the zero of the energy. Consider as boundary conditions the three types: (i) potential well with infinite walls; (ii) potential well with finite walls; (iii) periodic boundary condition. We shall elaborate here on the first case, as the other cases differ only in numerical detail, except of course[11] for the possibility of a degeneracy for the third case.

For the first case, the condition for the function is

$$\Psi(0) = \Psi(L) = 0 \ . \tag{2.3}$$

The general solution of Eq. (2.1), up to a normalization constant, is

$$\Psi(x) = \alpha\,\mathrm{Ai}(Z) + \beta\,\mathrm{Bi}(Z) \ . \tag{2.4}$$

Equation (2.3) implies (by solution of the secular equation) the condition

$$\mathrm{Ai}(-\alpha_1^{-2/3}\tilde{\epsilon})\,\mathrm{Bi}(\alpha_1^{1/3}L - \alpha_1^{-2/3}\tilde{\epsilon}) = \mathrm{Bi}(-\alpha_1^{-2/3}\tilde{\epsilon})\,\mathrm{Ai}(\alpha_1^{1/3}L - \alpha_1^{-2/3}\tilde{\epsilon}) \ . \tag{2.5}$$

Equation (2.5) is the equation for the eigenvalues of the energy, which are discrete for this case; it can be solved numerically. We shall here only indicate our results for limiting cases, in which analytic results exist.

Case (a): $\epsilon \ll eEL$, i.e., low-lying levels for high voltage differences on the crystal. In this case we neglect $\tilde{\epsilon}\alpha_1^{-2/3}$ with respect to $\alpha_1^{1/3}L$. If we also assume $\alpha_1^{1/3}L \gg 1$ (for an electric field of 1 V/cm, L should be greater than 10^{-5} cm for this condition to be satisfied), we get from (2.5), using the asymptotic forms for the Airy functions,[12] the approximate condition

$$2\exp(\tfrac{4}{3}\alpha_1^{1/2}L^{3/2})\,\mathrm{Ai}(-\alpha_1^{-2/3}\tilde{\epsilon}) = \mathrm{Bi}(-\alpha_1^{-2/3}\tilde{\epsilon}) \ .$$

The exponential on the left-hand side is much larger (for the above-mentioned condition) than $\mathrm{Bi}(-\alpha_1^{-2/3}\tilde{\epsilon})$ which is oscillatory,[12] so the condition for the eigenvalues resolves approximately to

$$\mathrm{Ai}(-\alpha_1^{-2/3}\tilde{\epsilon}) = 0 \ . \tag{2.6}$$

From the table of zeros of the Airy function (p. 478 in Ref. 12) we get (Fig. 2) the low-lying energy levels for this case. As should be anticipated the results here agree with the semiinfinite case (see, e.g., Ref. 13). For the levels further up [but still with condition (a)], namely, for $\alpha_1^{-2/3}\tilde{\epsilon} \gg 1$ (which happens for an electric field of 1 V/cm for $\epsilon > 10^{-5}$ eV and for an electric field of 10^5 V/cm for $\epsilon > 0.02$ eV), the result can be given by the asymptotic expression[12] for Ai and to first approximation,

$$\sin[\tfrac{2}{3}(\alpha_1^{-2/3}\tilde{\epsilon})^{3/2} + \tfrac{1}{4}\pi] = 0$$

or

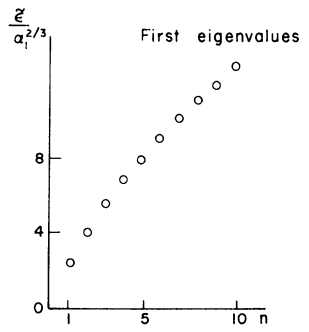

FIG. 2. First ten eigenvalues for the empty lattice in a constant electric field, given by the nodes g_n of $\mathrm{Ai}(x)$. The quantity $\tilde{\epsilon}/\alpha_1^{2/3}$ is in nondimensional units; see Eq. (2.7).

$$\tilde{\epsilon}_n = [\tfrac{3}{2}\pi\alpha_1(n-\tfrac{1}{4})]^{2/3} . \quad (2.7)$$

Now, for $n \gg 1$, this becomes

$$\epsilon_n \simeq CE^{2/3}n^{2/3} , \quad (2.8)$$

where

$$C = \tfrac{1}{2}(\hbar^2 3\pi e/m^{1/2})^{2/3} .$$

A simple physical way to get the dependence of ϵ_n on n and E is given in Appendix A.

The energy difference between levels decreases with n. From Eq. (2.8), we have

$$\epsilon_n - \epsilon_{n-1} = \tfrac{2}{3} CE^{2/3}n^{-1/3} \quad (2.9)$$

so that the "density of states" is approximately

$$\Delta n/\Delta\epsilon = (3/2C)(n^{1/3}/E^{2/3}) . \quad (2.10)$$

This result can be understood qualitatively as follows:

We are looking for solutions vanishing for $x=0$. The oscillatory behavior of the functions exists only for $x<l$ (Fig. 1), so if we start from $x=l$ with approximately the same amplitude, and going to the left, we want the function to vanish for $x=0$, we get the following: (i) The smaller the E, the faster is the change in l, as we go up with energy, so the easier it is to put another oscillation period into the wave function. (ii) For larger n, the number of periods in l gets larger, and the period of the wave function gets smaller so it is again easier to add one more period.

To get the eigenfunctions for this case we need (except for normalization) the ratio β/α. Now, according to (2.3), we must have

$$\alpha\,\mathrm{Ai}(\alpha_1^{1/3}L - \tilde{\epsilon}/\alpha_1^{2/3}) + \beta\,\mathrm{Bi}(\alpha_1^{1/3}L - \tilde{\epsilon}/\alpha_1^{2/3}) = 0$$

or, with condition (a),

$$\alpha\,\mathrm{Ai}(\alpha_1^{1/3}L) + \beta\,\mathrm{Bi}(\alpha_1^{1/3}L) = 0 .$$

Thus, in this range, the ratio does not depend on the energy, and is given by

$$\frac{\beta}{\alpha} = -\frac{\mathrm{Ai}(\alpha_1^{1/3}L)}{\mathrm{Bi}(\alpha_1^{1/3}L)} \approx -\tfrac{1}{2}\exp[-\tfrac{4}{3}(\alpha_1^{1/3}L)^{3/2}] , \quad (2.11)$$

where use has again been made of the asymptotic formulas for Ai and Bi for large $\alpha_1^{1/3}L$. Up to a normalization constant (which is calculated in Appendix B), we have

$$\Psi_n(x) = \mathrm{Ai}(\alpha_1^{1/3}L - \tilde{\epsilon}_n/\alpha_1^{2/3}) - \tfrac{1}{2}\exp[-\tfrac{4}{3}(\alpha_1^{1/3}L)^{3/2}]\,\mathrm{Bi}(\alpha_1^{1/3}L - \tilde{\epsilon}_n/\alpha_1^{2/3}) . \quad (2.12)$$

Case (b): $\epsilon \gg eEL$ very small electric field, nearly free electrons. Using the asymptotic expressions (10.4.60)–(10.4.63) of Ref. 12 we get from condition (2.5) to first order in $\alpha_1^{2/3}/\tilde{\epsilon}$

$$\sin(\zeta+\tfrac{1}{4}\pi)\cos(\zeta_1+\tfrac{1}{4}\pi) + C_1\left(\frac{1}{\zeta_1} - \frac{1}{\zeta}\right)\cos(\zeta_1-\zeta) = \cos(\zeta+\tfrac{1}{4}\pi)\sin(\zeta_1+\tfrac{1}{4}\pi) , \quad (2.13)$$

where

$$\zeta = \tfrac{2}{3}(\tilde{\epsilon}\alpha_1^{-2/3})^{3/2}, \quad \zeta_1 = \tfrac{2}{3}(\tilde{\epsilon}\alpha_1^{-2/3} - \alpha_1^{1/3}L)^{3/2} ,$$

and $C_1 = 15/216$.

The second term on the left-hand side in Eq. (2.13) is of the order of $(\zeta-\zeta_1)/\zeta^2$ and can be neglected.[14]

Thus we get in this case approximately

$$\tan(\zeta+\tfrac{1}{4}\pi) = \tan(\zeta_1+\tfrac{1}{4}\pi) \quad \text{or} \quad \zeta_1 - \zeta = n\pi .$$

Using the definition of ζ_1, ζ and condition (b) we get as the result for this case

$$\tilde{\epsilon}^{1/2} = n\pi/L , \quad (2.14)$$

which is equivalent to the case of free electrons in an infinitely deep well, as expected.

This complete solution for a free electron in a finite-range electric field is, to our knowledge, presented here for the first time.

III. MATHIEU-TYPE CRYSTAL IN AN ELECTRIC FIELD

We treat here a one-dimensional "crystal" whose periodic potential is a simple cosine function subjected to an external electric field. Before considering this case it is instructive to recall some concepts of the case of an infinite "crystal" with this type of periodic potential in the absence of the electric field which was treated by Slater.[15]

In the zero-field case the Bloch electron behaves according to the following Schrödinger time-independent equation (Mathieu-type differential equation):

$$[p^2/2m + 2W_1(1-\cos 2\pi x/d)]\varphi(x) = \epsilon_0\varphi(x) , \quad (3.1)$$

where d is the lattice constant and $4W_1$ is the height of the periodic potential in energy units. The minima of the periodic potential occur at $x=nd$, $n=0, \pm1, \pm2, \ldots$. The solutions of (3.1) are extensively discussed in Ref. 15 where it is shown that the eigenvalues for the energy do show many properties of a real crystal, e.g., they appear in bands of allowed levels separated by gaps of forbidden levels. The results were obtained under boundary conditions at infinity, namely, that the function in momentum space (in fact, the Fourier transform of the Wannier function of the problem) falls off exponentially at $x=\pm\infty$. The eigenfunctions, except for the charge distribution in momentum space which depends strongly on the shape of the potential (see Ref. 15, p. 818), show also many features of real crystals. Recalling in addition that the form of the potential in (3.1) can always be seen as the first terms in the expansion of

the real potential, we see that it is reasonable to treat such a model and expect to get results which are close to the natural ones.

We therefore treat here this type of crystal with two additional changes. The first is that we take a finite crystal (and thus we are able to check the influence of boundary conditions on the problem) and the second is that we add the potential eEx to the periodic one, to represent the external electric field. The differential equation we deal with is

$$[p^2/2m + 2W_1(1 - \cos 2\pi x/d) + eEx]\Psi(x) = \epsilon\Psi(x) \ . \tag{3.2}$$

In order to have a connection with Slater's results for the zero-field case, we transfer to new nondimensional variables, and get

$$d^2\Psi/d\omega^2 + (\mu + \tfrac{1}{2}S\cos 2\omega)\Psi - \alpha\omega\Psi = 0 \ , \tag{3.3}$$

where

$$\omega = \pi x/d, \quad S = 32W_1md^2/\hbar^2, \quad \mu = \epsilon' S^{1/2} - \tfrac{1}{2}S,$$

$$\epsilon' = (2m/W_1)^{1/2}\epsilon d/h, \qquad \alpha = 2md^3/\hbar^2\pi^3 eE$$

[compare with Eqs. (9)–(11) in Ref. 15].

In order to obtain a feeling for these variables, let us calculate a specific example: Suppose we have a crystal with $d = 5$ Å, then $\hbar^2/2md^2 = 0.125$ eV, $S = 3.2W_1$ (eV) measures the potential height (if we stay with the same d). As W_1 gives an approximation to the energy gap (say by the tight-binding approximation), then if we want the latter to be of the order of 1 eV we need S of the order 1. $\alpha \simeq 1.3 \times 10^{-8}E$ (V/cm) measures the field intensity. For big fields, say 10^5 V/cm, α is of the order of 10^{-3}. As we shall see later, for the sake of band broadening, the important parameter is the voltage drop over the sample and not merely the field. Hence a better parameter to consider is perhaps $\alpha\pi L/d = \alpha\pi N$, where L is the length of the crystal ($L = Nd$). $\epsilon' \simeq 0.4\epsilon W_1^{-1/2}$, where the units are in eV for ϵ and W_1. Conversely, from the results we get for ϵ', we can retrieve ϵ by $\epsilon = 2.5\sqrt{W}_1\epsilon'$.

As boundary conditions (BC), we use the following three types:

(i) *Infinitely high potential well.* Our crystal stretches between 0 and L, so these BC are equivalent to $\Psi(0) = \Psi(L) = 0$.

(ii) *Finite potential well.* We assume that for $x < 0$ and $x > L$, $V = V_0$ and that, dealing with bounded states, we have $\epsilon < V_0$. In this case the solutions outside the crystal are decreasing exponentials: $\Psi(x \le 0) = Ae^{\bar{\alpha}x}$, $\Psi(x \ge L) = Be^{-\bar{\alpha}x}$, where $\bar{\alpha} = [2m(V_0 - \epsilon)/\hbar^2]^{1/2}$.

Thus these BC are equivalent to

$$\frac{\partial\Psi}{\partial x}(0) - \bar{\alpha}\Psi(0) = 0 \ , \quad \frac{\partial\Psi}{\partial x}(L) + \bar{\alpha}\Psi(L) = 0 \ . \tag{3.4}$$

(iii) *"Periodic" boundary conditions* (PBC). As has been discussed earlier, [8] the full periodic BC, i.e., $\Psi(x+L) = \Psi(x)$, although appropriate for the crystal without the field, does not give a solution at all for the $E \neq 0$ case, and in this case we can use only the appropriate PBC, namely,

$$\Psi(0) = \Psi(L) \ , \qquad \frac{\partial\Psi}{\partial x}(0) = \frac{\partial\Psi}{\partial x}(L) \ . \tag{3.5}$$

These three types of BC are special cases[11] of the "homogeneous BC" for which there exist solutions with allowed eigenvalues and eigenfunctions.

Several results can be predicted at this stage. Considering Eq. (3.2), we see immediately that there exist two well-defined limiting cases.

The first occurs when E is zero or very small (in fact, the potential difference, and not the field, should be very small). In this case we have the problem discussed by Slater, [15] namely, the Mathieu equation, except that we treat a finite crystal and thus will be able to see the influence of the different BC. As mentioned in Sec. II the only case in which we can have a degeneracy of the eigenfunction is type (iii), consisting of a differential equation with periodic coefficients and PBC. [8] In the other cases, we expect no degeneracy, even though the coefficients are appropriate, as the BC are not adequate for that. It follows that we can have "current-carrying states" only for the type (iii) using the following argument: Having a real one-dimensional second-order differential equation, if we do not have a degeneracy for a certain energy, the solution (we have only one in this case) can always be chosen to be real, and the current operator

$$J = \frac{\hbar}{2mi}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right) \tag{3.6}$$

will obviously be zero. This argument means that in order to build Bloch states (which are current-carrying states) we need in this case a finite one-dimensional crystal, a PBC. Thus it is evident that the eigenfunctions are very sensitive to the form of the BC. On the other hand, for the eigenvalues the situation has not been completely clear. For the case of lattice vibrations, there exists a proof[16] that the effect of BC on the spectrum is negligible. It was inferred (though without a rigorous proof) that the same negligible dependence on the BC would also be valid for the electronic spectrum. In Appendix D, we extend the above-mentioned proof[16] to this case of electronic states in crystals and the results do agree with the above-mentioned previous predictions. Having at our disposal the Mathieu-type model, we will be able to verify these results also in a quantitative way. In fact, from Appendix D, we have three upper limits for the changes in the spectra with the differing types of BC for this model, and these will be verified with

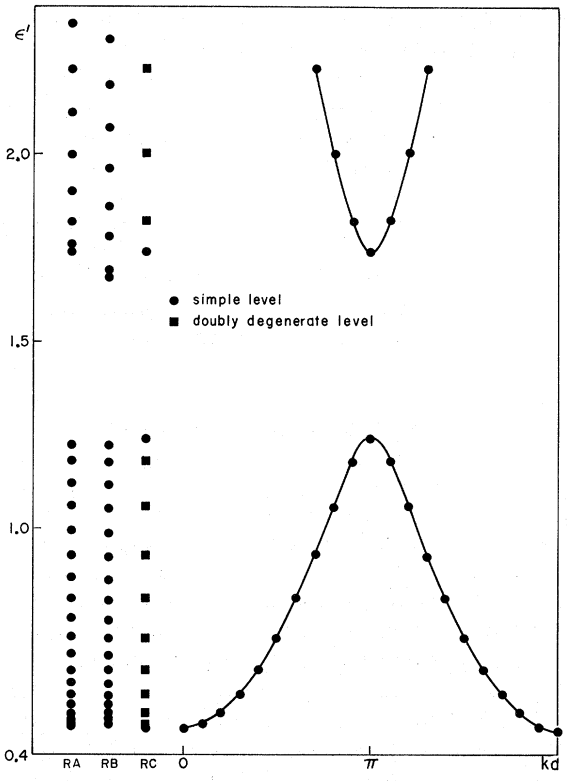

FIG. 3. Discrete energy levels in the zero-field case. ϵ' is in nondimensional units; see Eq. (3.3). Left-hand side: effect of BC on the spectrum (lowest band and part of next band); R_a, infinite well; R_b, finite well; R_c, PBC [Eq. (3.5)]. Right-hand side: ϵ' vs k for the periodic case; degenerate levels appear twice, for kd and for $2\pi - kd$.

the numerical results.

The second limiting case we have is when E is very large (eEL—which turns out to be the important parameter—large compared with $4W_1$). In this case we can neglect the effect of the crystal field and we have the problem of a "free" particle in a finite electric field. This is the Airy problem, discussed[12] extensively by mathematicians. Here again the problem explored in the past is the infinite one, where we know that there are solutions for every energy: Those which vanish at $\pm\infty$ are the Ai's and the second solutions which increase as $e^{x^{3/2}}$ at $+\infty$ are the Bi's. The problem of the finite-range empty crystal in an electric field is dealt with in Sec. II, and, as was shown, we get only discrete allowed energies ranging from 0 upwards. These levels occur, for low energies, at approximately $\epsilon_n = (\hbar^2/2m)^{1/3}(Ee)^{2/3}g_n$, where g_n are the nodes of Ai. They behave approximately proportional to $(n-\frac{1}{4})^{2/3}$ [see Fig. 2 and Eq. (2.7)]. Here we expect to get this behavior for the large E's when the term with the field in (3.2) is the dominant one. In this case the crystal manifests itself only through the BC. It is perhaps worthwhile to note that we solve for the electrostatic *finite* case and so do not expect to get (for large E) a behavior of a "free" electron in an electric field, but that of an "empty crystal," with no current.

In the numerical calculations several crystal lengths and the three types of BC [(i)–(iii)] were tried. The eigenvalues and eigenfunctions were obtained both with the field and without it. Some details of the numerical calculation appear in Appendix C.

For the zero-field case, we use Bloch theorem for type (iii) BC, a theorem which in this case is equivalent to that for an infinite crystal. This theorem states that there exist solutions to the differential equation having the property

$$\Psi_k(x+d) = e^{ikd}\Psi_k(x)\,,$$

where $k = 2\pi m/L$; $m = 0, 1, \ldots, N-1$ are the quasi-momentum vectors of the first Brillouin zone, and the fact that there exist only N allowed values for k stems from the BC (we need $e^{ikL} = 1$). Figure 3 gives these results for the "undisturbed" crystal. It is interesting to note some of the features, especially those concerning the BC predicted above. First, we see that the only degenerate case is the one with type (iii) BC, which can be interpreted as following from $\epsilon(k) = \epsilon(-k)$ in the Bloch picture of the problem: The only levels which are not degenerate in this case are the extreme ones, pertaining to $k = 0$, $2\pi/d$ (i.e., the ends of the Brillouin zone). We know from the mathematical analysis[12] that the second (independent) solution of the equation in this case diverges. Second, the number of levels in a band is seen to be N, agreeing with the N allowed values of m as discussed above. Third, the change in the number of eigenvalues in any interval is seen to obey the result obtained in Appendix D, namely, that this change is at most 1 between types (i) and (iii) and at most 2 between (i) and (ii). Next, we observe that the range (around the extremum) of validity of the k^2 proportionality of the spectrum ϵ [a formula we shall use in Sec. IV when we deal with the effective-mass approximation (EMA)] is much larger for the lower band than for the upper band. This implies that the EMA in its simplest form [where we use $-(\hbar^2/2m^*)\nabla^2$ as the approximate operator which takes into account the periodic potential] will apply for a larger range in the upper band.

The effect of the length of the crystal on the distribution of levels was negligible as seen in Fig. 4, where crystals of 10, 20, and 60 unit lengths are compared. Except for a change in the number of levels in a band according to N, there are no noticeable changes in the "spectrum." This fact can be easily understood since by Bloch's theorem [suppose we deal with type (iii) BC] for a crystal

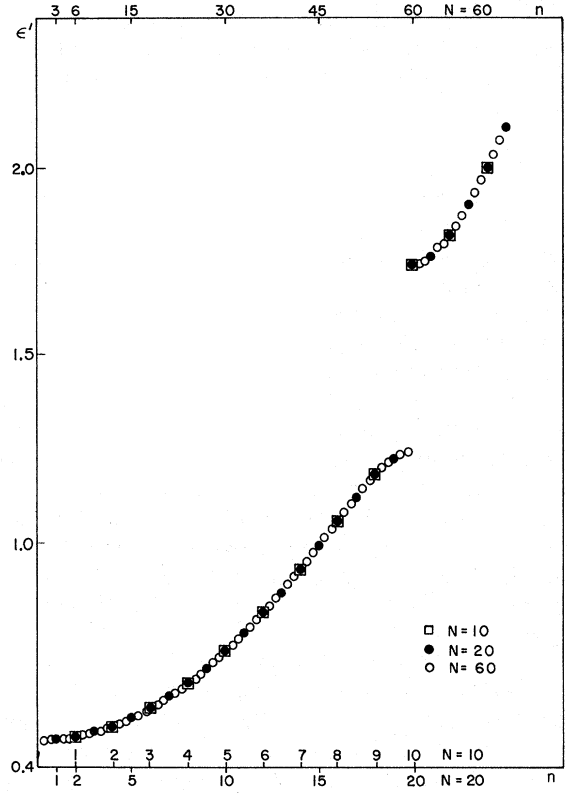

FIG. 4. Plot of energy levels [in the nondimensional units of Eq. (3.3)] for the zero-field case for the type (i) BC vs the number of the state n for three lengths of the crystal: $N=10$, 20, 60. (N is the number of unit cells in the crystal and also the number of levels in a band.)

of length L, every solution has the form

$$\Psi_{L,j}(x+d)=e^{i2\pi d m_j/L}\Psi_L(x)\ ,\quad m_j=0,1,\ldots,N_j-1\ .$$

Now, consider two crystals of lengths L and pL accordingly, where p is an integer. There will be N solutions for the first one with $m=0,1,\ldots,N-1$ and pN solutions for the second $[m'=0,1,\ldots,(pN-1)]$. Those solutions for the second crystals which have $m'=pm$ will have an identical differential equation and an identical BC (on a unit cell) and thus an identical solution. (This is the case for zero field, but in the presence of the field the situation is obviously different since for $E\neq 0$ the Bloch theorem is not valid.)

With the application of the field, the distribution of levels changes. Figures 5–7 show what happens. These give the energy as a function of n, a number monitoring the levels, beginning with the lowest. For the zero-field case this number has a direct connection with k (see Fig. 3 and Sec. IV), while the concept of k loses its meaning in the case of the crystal in the field.

For $S=1$ (small periodic potential height and thus small energy gap), Fig. 5 shows several interesting properties: It is seen that the "beginning," i.e., the lowest part, of each band changes very slightly, while the upper part (in this case of the first band) increases with the field. This increase for small fields seems almost proportional to E. The same calculation was carried out for crystals of different lengths and the increase was proportional to the length. The outcome indicates, of course, that this increase is approximately proportional to the voltage drop across the crystal, a result which can be obtained analytically for the EMA[17] (see also Sec. IV). The net result of the very small increase in the beginning of the upper band and the increase in the "top" of the lower band is that the forbidden energy gap is decreased with the voltage. A similar behavior is seen (Fig. 6) for $S=5$ (relatively high periodic potential), except that there evidently the influence of the voltage

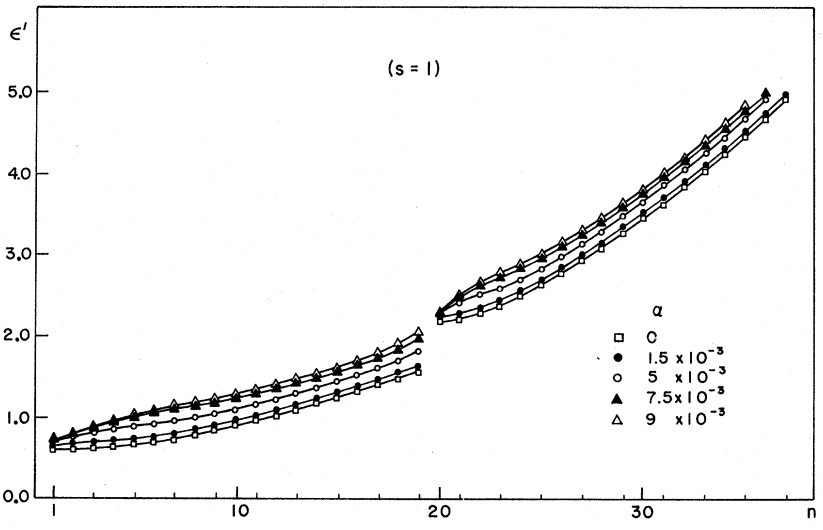

FIG. 5. Energy spectrum changes with respect to the electric field. The band gap is between levels 19 and 20. S[the parameter measuring the crystal-field strength; see Eq. (3.3)] is small (=1). α measures the electric field strength; see Eq. (3.3). The energy (ϵ') is measured in the nondimensional units of Eq. (3.3). The voltage drop (V) on the sample in the same units is given by $V=20\pi\alpha$ (e.g., for $\alpha=5\times10^{-3}$ we have $V=0.314$; compare with the zero-field energy gap 0.68 in this case).

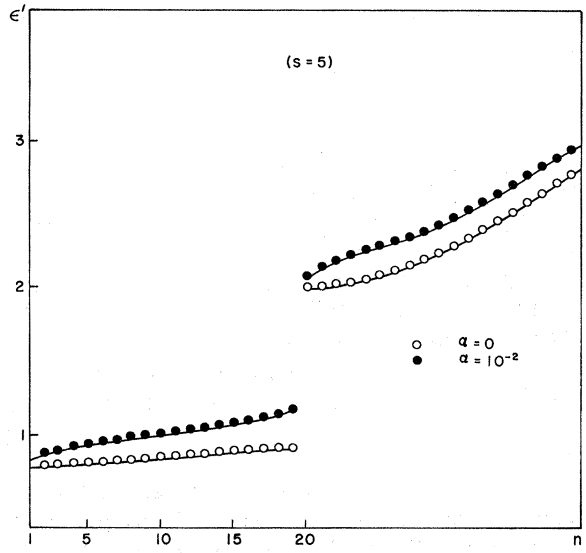

FIG. 6. Energy spectrum changes with the field for a relatively high ($S=5$) crystal potential (high-energy gap). ϵ' in the nondimensional units [see Eq. (3.3)].

drop on the crystal is smaller than that for $S=1$, the relevant parameter being the ratio of this voltage drop to the forbidden breadth.

The density of states changes too. For $E=0$ we have a distribution of states which is approximately parabolic near the edges of the bands, a fact stemming from Bloch's theorem. For very high fields (in the sense of high potential differences with respect to the gap or the periodic potential barrier) the crystal field is negligible in comparison with the field-containing term and we have an approximate finite Airy problem. The eigenvalues for this problem with type (i) BC and for energies which are not the lowest in the band are given (in Slater's units) by

$$\epsilon_n' S^{1/2}/\alpha^{2/3} \simeq [\tfrac{3}{8}\pi(4n-1)]^{2/3} . \qquad (3.4')$$

Figure 7 gives the comparison for the energies of the finite crystal in high electric fields with the right-hand side of (3.4′). The convergence to the right-hand side is apparent.

Absence of the Stark ladder effect is striking in all the results (Figs. 5–7). In our calculations it categorically does not appear. The arguments for its appearance would have predicted a set of evenly spaced discrete levels ranging over the whole spectrum in the presence of the electric field. *No* such levels are seen. The discreteness of the spectrum in our treatment comes from the finiteness of the sample and has nothing whatsoever to do with the Stark ladder arguments. For strong field this discrete-level structure can perhaps be detected experimentally.

Now let us turn to the eigenfunctions. In Fig. 8 the eigenfunctions for the zero-field case for type (i) BC are given. It is seen that for the lower part and the upper part of each band, in agreement with the EMA[18] (see also Sec. IV), they behave like a product of two functions. One is the usual Mathieu function[12] which is the solution of this equation (3.1) at the bottom (or top) of the band and the other comes from the "well" with the PBC, and consists of sines or cosines. For the first band, the appropriate Mathieu function is $ce_0(z)$, the structure of which is seen in Fig. 20.2 of Ref. 12. We see there that this function does not have any nodes in

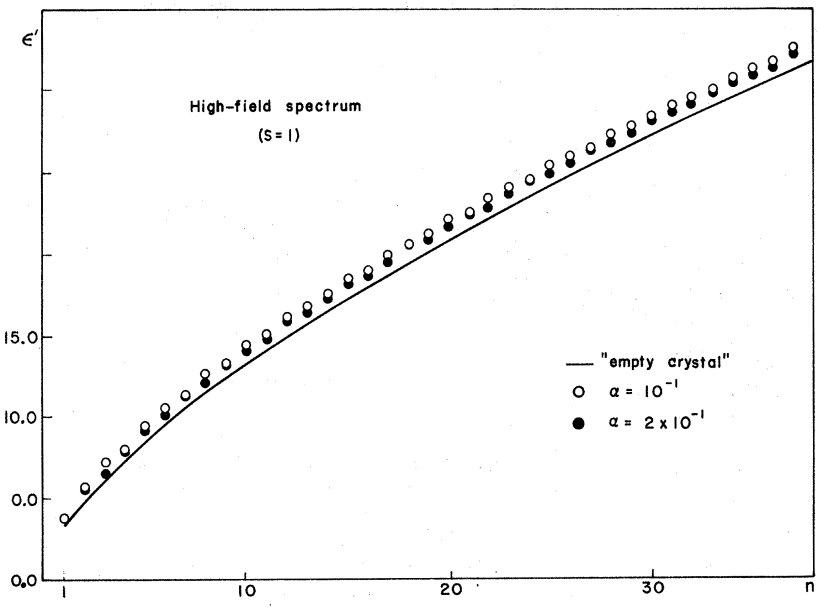

FIG. 7. ϵ' (in the nondimensional units of $\alpha^{2/3}/S^{1/2}$) vs n for high fields. The full line is the empty crystal in an electric field case [the right-hand side of Eq. (3.4)]. As the field increases from $\alpha=10^{-1}$ to $\alpha=2\times10^{-1}$ the spectrum approaches the full line.

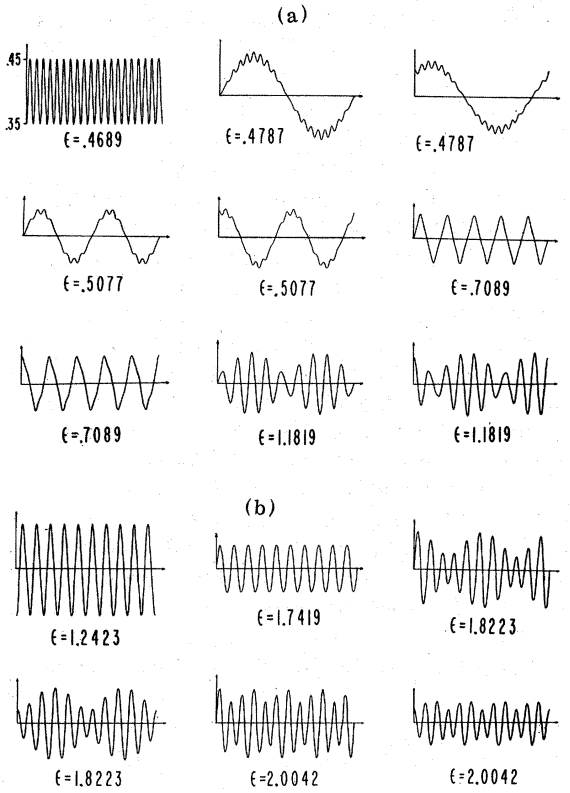

FIG. 8. Wave functions for a finite-range crystal with no electric field ($\alpha = 0$); type (iii) (periodic) BC. Several functions belonging to energies in the lower and upper parts of the first band, and in the lower part of the second band are shown, as well as several eigenfunctions from the middle of the first band. The lowest and the uppermost levels in each band are nondegenerate while the others are doubly degenerate (pertaining to kd and to $2\pi - kd$).

the whole interval. In fact, by Eq. 20.2.27 there we can calculate the ratio of the highest value to the lowest value of this function during a single oscillation. For small q (which in our notation is equal to $\frac{1}{4}S$), we have

$$\mathrm{ce}_0(z, q) \simeq 2^{-1/2}(1 - \tfrac{1}{2} q \cos 2z) \ . \qquad (3.5')$$

For $S = 1$, the change in amplitude in one cycle is $\frac{1}{4}$ of its maximum. Consider now the first eigenfunction appearing in Fig. 8 (that for $\epsilon' = 0.4689$). It has as a multiplier the first function of the "well" which is a constant, and thus the oscillations of the other multiplier, namely $\mathrm{ce}_0(\omega)$, are observed. It is evident that the oscillations are approximately $\frac{1}{4}$ of the height of the function, in agreement with (3.5'). The next level ($\epsilon' = 0.4787$) is degenerate, and we have $\cos(2\pi/L)\omega$ and $\sin(2\pi/L)\omega$ multiplying the Mathieu function. Again the oscillations constitute about $\frac{1}{4}$ of the height. The two degenerate functions can, of course, be combined to give the Bloch-type traveling waves to the right or to the left (which are degenerate too).

This "effective-mass" interpretation of the behavior of the functions can go on for the next several values of ϵ'. Then, for higher states, the functions become more complex, but even here one can still perceive, albeit vaguely, the "product"—EMA behavior. Starting now from the top of the first band ($\epsilon' = +1.2423$), the level is again nondegenerate, and the Mathieu function multiplying the cosine function [$\cos(2\pi/L)\omega \times \frac{1}{2}N = \cos(\pi\omega/d) = \cos\omega$ in our choice of units] is the off one: se_1. That we have indeed this kind of behavior can easily be seen by noting from Eq. 20.2.27 of Ref. 12 for small q

$$\mathrm{se}_1(z, q) \simeq \sin z \ . \qquad (3.7)$$

Thus the product is $\sin z \cos z = \frac{1}{2}\sin 2z$, and we note that the number of oscillations in the whole length of the crystal is one-half of that for $\epsilon' = 0.4787$ (10 instead of 20). In fact, we have a change of origin from (3.7) because the "well" function is an admixture of $\sin\omega$ and $\cos\omega$. The same product behavior discussed above is seen for the first several functions when we start from the top and go down in energy, e.g., for $\epsilon' = 1.1819$ the function behaves like $\cos 0.9\omega$ or $\sin 0.9\omega$ times $\mathrm{se}_1(\omega) \simeq \sin\omega$. The same argument applies for the beginning of the upper band, the appropriate Mathieu function now being $\mathrm{ce}_1(\omega)$.

Turning now to the case where the field is present, we see in Fig. 9 the situation for a moderate field ($\alpha = 10^{-2}$ or $V \simeq 0.6$, which is of the order of the band gap). There is no longer any degeneracy because the coefficients of the differential equation are not periodic. The label for the energy eigenvalues is now simply $n = 1, 2, \ldots$, as now there is no meaning to the wave vector k. We see that here too the graphs can be interpreted qualitatively with

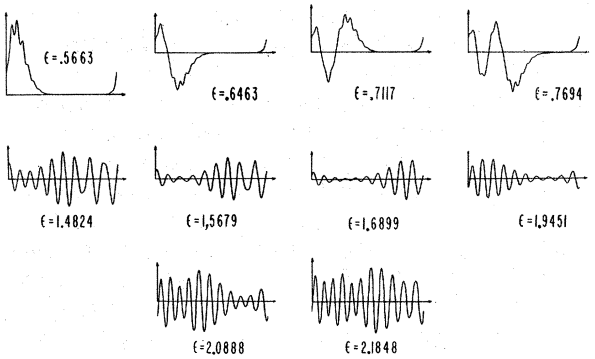

FIG. 9. Several wave functions of a crystal in the presence of a finite-range electric field ($\alpha = 0.02$); type (iii) BC. Again (as in Fig. 8) only functions belonging to energies in the band edges plus some belonging to the middle of the first band are shown. The degeneracy is lifted by the field, thus all levels are nondegenerate.

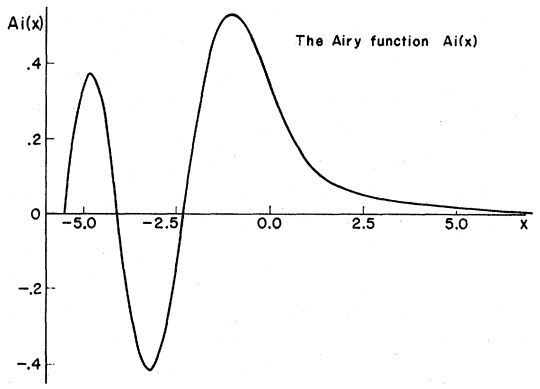

FIG. 10. Airy function Ai(x) as a function of x. The two types of behavior, oscillatory for $x<0$ and exponential ($e^{-x^{3/2}}$) for $x \gg 0$, are manifest.

the help of the EMA. The first graphs in Fig. 9 strongly resemble a product of $ce_0(x)$ (which we discussed above), with another function, except that now this second function is an Airy function consisting of a linear combination of Ai and Bi, such that the function fulfills the type (iii) BC. Such a function (see Sec. II) is almost identical to Ai along most of the interval $0-L$ (the contribution from Bi becomes noticeable only in the immediate vicinity of $x=L$). We can compare the behavior in Fig. 9 with that of a simple Ai function (Fig. 10). The boundary condition [type (i), say] on the left-hand side means (Sec. II) that the comparison should start from a node of Ai. The other limit ($x=L$) is a length L to the right of this node (which is labeled $x=0$). In our case for a small number of nodes of Ai (the starting point moves so as to include more nodes for higher levels) in the interval $0-L$, L is large, and so the comparison can be made with Ai between $-g_s$ (node No. s) and ∞. Thus for $\epsilon'=0.5663$ in Fig. 9 we have approximately the Airy function with no nodes multiplying $ce_0(\omega)$, etc. Now, we still retain (even for such a comparatively high field) the EMA behavior near the forbidden gap. For $\epsilon'=1.5899$ and $\epsilon'=1.9451$, the two ends of the energy gap, we have again an Airy function of no nodes modulating the Mathieu function se_1 and ce_1, respectively, as for the case with no field). The difference between the modulating functions in the two sides of the band gap is that one Airy function goes from left to right while the other goes from right to left because the effective mass in the upper limit of the lower band is negative. This is discussed thoroughly in Ref. 17 (see also Sec. IV of this paper). Going in both directions from the ends of the band (from 1.6899 down in energy and from 1.9451 upwards), the EMA behavior is seen to persist for a while, Airy functions with increasing number of nodes appearing sequentially as we go away from the band-gap boundaries.

IV. DIRECT AND EMA-TYPE CALCULATIONS OF ENERGY EIGENVALUES

The invalidity of the EMA for the time-independent solutions of the infinite crystal in an external electric field[19] can easily be shown[20] by the following argument: The EMA states that the eigenvalues and eigenfunctions of the Schrödinger equation in the presence of a perturbation by a "gentle potential"[18] can be obtained by solving the effective equation, in which the periodic crystalline potential does not appear and instead the mass parameter is changed. In the proof of the validity of this approximation it is required[20] that the Fourier transform of the functions which are the solutions for this "effective Schrödinger equation" be such that it would be possible to represent the function by a small number of $\vec{k}$ vectors or, to put it differently, that the volume in $\vec{k}$ space needed for the development of that function be much smaller than the volume of the Brillouin zone. Now, for the infinite one-dimensional crystal, the Fourier transform of the appropriate function, namely the Airy function Ai(x), is given[21] by

$$\mathrm{Ai}(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}e^{ik^3/3}\,dk \tag{4.1}$$

and *no* range of k can be discarded.

For the finite crystal, however, this is no longer true, and in fact it can be proved[17] that for voltages small compared to the band gap, the EMA can be valid. In the Mathieu-type model we compare numerically the accurate results with those of the EMA for the energy levels. Our results are given in nondimensional variables of Slater type and in order to facilitate the calculations with the EMA we formulate it in a different way, a way which may be of help in more general cases: Suppose we have an equation

$$\frac{d^2\Psi}{dx^2}-[V(x)+U(x)]\Psi+\epsilon\Psi=0\,, \tag{4.2}$$

where $V(x)$ is periodic with a period d and $U(x)$ is a "gentle" potential, and with BC given, say, at $x=0$ and at $x=L=Nd$. We can get an approximate solution to (4.2) if we know the solutions for the "unperturbed" equation

$$\frac{d^2\varphi}{dx^2}-V(x)\varphi-\bar{\epsilon}\varphi=0 \tag{4.3}$$

with the same BC, provided the energy spectrum consists of allowed bands separated by forbidden gaps and inside each band the eigenvalues depend quadratically on n, the level-number parameter, i.e., $\bar{\epsilon}_n=\bar{\epsilon}_0+qn^2$, where $\bar{\epsilon}_n$, $\bar{\epsilon}_0$ pertain to the same band. Now, if the EMA is valid we can get a solution to (4.2) by considering instead the effective equation

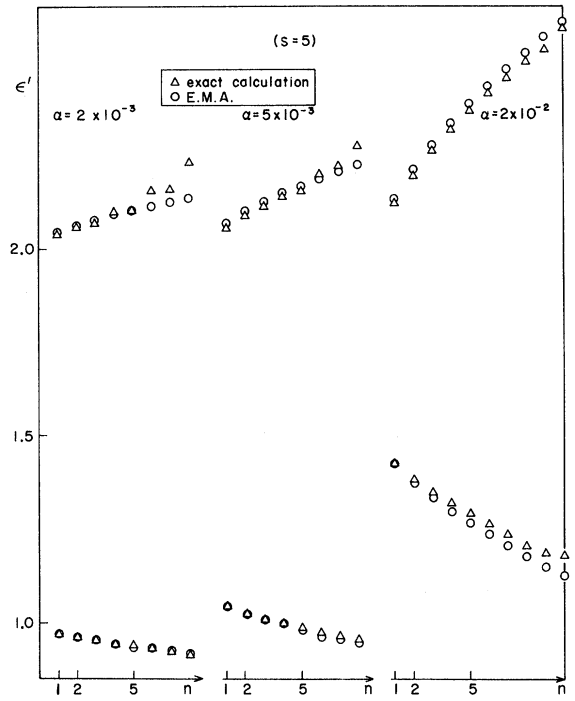

FIG. 11. Exact and EMA-type spectra for three different fields, $\alpha = 2\times10^{-3}$, 5×10^{-3}, 2×10^{-2}. The bands are arranged here such that the $n=1$ levels will be those (for the upper and lower bands) levels which are closest to the gap. Only the first few levels ($1\leq n\leq 8$, 10) are shown. The EMA is seen to hold for moderate fields almost till the middle of the bands. ϵ' is in the nondimensional units of Eq. (3.3).

$$\bar{q}\frac{d^2\chi}{dx^2} - U(x)\chi + (\epsilon - \epsilon_0)\chi = 0 \qquad (4.4)$$

with the same BC, where $\bar{q} = q(L/2\pi)^2$. This formulation of the EMA can be obtained from the usual form simply by multiplying (4.2) by $-\hbar^2/2m$ and by using the definition of k, namely $k_n = (2\pi n/L)$. The curvature $\bar{q}$ is equivalent to m/m^* in the usual form of the EMA.

In our problem the period d is π [see (3.3)], $L = N\pi$; $\bar{\epsilon} = S^{1/2}\epsilon'$. We solve (3.3) numerically for $\alpha = 0$ and get the spectrum. From the behavior of ϵ' with the level number n we derive q, and (4.4) will become (for $N = 20$)

$$100q\frac{d^2\chi}{d\omega^2} - \alpha\omega\chi + S^{1/2}\epsilon\chi = 0 \qquad (4.5)$$

with boundaries $\omega = 0$, $\omega = 20\pi$. ϵ is measured with respect to the unperturbed case. This again is an Airy-type equation. The solutions for positive $\bar{q}$ are

$$\Psi i\left(\frac{\alpha^{1/3}\omega}{\bar{q}^{-1/3}} - \frac{\epsilon S^{1/2}}{\bar{q}^{-1/3}\alpha^{2/3}}\right) , \qquad (4.6)$$

where Ψi is a linear combination of Ai and Bi, such that the BC are fulfilled. If we demand, e.g., type (i) BC, then for the upper band this gives approximately (see Sec. II)

$$\epsilon_s = \bar{\epsilon}_0 + (\alpha^{2/3}/S^{1/2})\bar{q}^{-1/3}g_s \qquad \text{(upper band)}, \qquad (4.7)$$

where g_s are the places where $\mathrm{Ai}(x)$ has nodes.

For the lower band, $\bar{q}$ is negative, say $= -\mu$, and instead of (4.6) we get as the solutions of (4.5)

$$\Psi i\left(\frac{\epsilon S^{1/2}}{\mu^{1/3}\alpha^{2/3}} - \frac{\alpha^{1/3}\omega}{\mu^{1/3}}\right) , \qquad (4.5')$$

which is the same function as (4.5) only going from right to left. Now the BC at $\omega = 0$ is approximately fulfilled for high-enough energies by the $e^{-x^{3/2}}$-type decay of $\mathrm{Ai}(x)$ for positive arguments, while the BC at $\omega = L$ gives here

$$\epsilon_s = \epsilon_0 + \frac{\alpha L}{S^{1/2}} - \frac{\mu^{1/3}\alpha^{2/3}}{S^{1/2}}g_s \qquad \text{(lower band)} . \qquad (4.8)$$

Now we can compare these approximate solutions (4.7) and (4.8) to the EMA equation with the exact eigenvalues obtained by solving the original equation (3.2). The results for $S = 5$ (which has a better parabolic behavior than $S = 1$) appear in Fig. 11. Although the original equation was carried out for type (iii) BC and the EMA for type (i), we see a very good fit for the two ways of calculation for a considerably large part of the bands, except for high electric fields (for $\alpha = 2\times10^{-2}$ the voltage difference across the sample, namely, $\alpha L/S^{1/2}$, is approximately one-half of the band gap). This quantitative result, combined with the foregoing qualitative discussion of the wave, provides a very good example for which the EMA is a very good approximation for an electron in a finite crystal in an external electric field.[17]

V. DISCUSSION

The empty-crystal calculation in the presence of an external constant electric field leads to a number of interesting results. It is shown that the non-Fourier-transformable second solution cannot be ignored (in the finite case) and gives rise to a completely different spectrum than in the infinite case. The eigenvalues have a lower bound and the high-energy solutions merge smoothly into the zero-field spectrum as they should.

The empty-lattice treatment indicates already that the influence of BC is crucially important in the "field" case. This trend is enhanced in the model calculation of Secs. III and IV. Considering the cases with and without the external field, we see that the situations are quite different. Without the field, if we add to the finite crystal another similar one, we can continue the physical param-

eters, which in this case are the potentials, continuously into the second crystal and get a reproduction of the first; whereas for the external-field case the length of the crystal is connected with the existence of a parameter, namely, the electric potential difference on it, which is of a distinct type. This parameter does not reproduce itself upon a repetition of the crystal, and in fact goes to $\pm\infty$ for inifinte crystals.

The numerical treatment of the Mathieu model has enabled us to get a clear and well-understood picture of the features of the problem. A large amount of useful details were brought forth. Concerning the eigenvalues the physical properties emerging were the following: (a) a linear decrease in the band gap with the voltage drop on the crystal, a decrease which may be responsible to the "electro-optic" effect; (b) a change in the density of states with the field, which for small voltage differences can be described by the EMA; (c) a complete absence of the formerly predicted Stark ladder spectrum. As important side results which were derived, let us mention the numerical verification of the extension of the BL theorem concerning the influence of BC on the spectral density and the partial answer to the question: "What is the minimal number of unit cells which can be called a crystal?" It is obvious that a number of the order of 10 is a lower bound. As for the eigenfunctions, the complex influence of the crystal field and the external electric field was shown. This intermingling was explained, for the range of eigenvalues near the band extrema, qualitatively by the EMA, while for other eigenvalues the behavior is more complex. Having calculated the energies and the eigenvectors, the whole problem of the dynamics for this model is in principle solved. In future publications we shall expand on this and try to calculate other properties of this model.

Finally, we should point out that several applications of the general treatment are now under study: the EMA to the energy eigenvalues and eigenfunctions and its validity[17]; calculation of optical absorption in the presence of the field and the Franz-Keldish[7] effect; Zener breakdown, and others. These are subjects for future publications.

ACKNOWLEDGMENTS

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APPENDIX A

A simple physical approximation to obtain the dependence of ϵ_n on n, Eq. (2.8), is the following: Suppose (Fig. 1) we solve a case of an equivalent square well, having a length l, which is given by ϵ_n and the electric field

$$eEL = \epsilon_n \,. \tag{A1}$$

The well-known result for the energy levels of the square well is

$$\epsilon_n = \frac{\hbar^2}{2m}\left(\frac{2\pi n}{l}\right)^2 = \frac{h^2}{2m}\,\frac{n^2}{l^2} \,. \tag{A2}$$

If we substitute l from (A1) we get

$$\epsilon_n = \left(\frac{h^2e^2}{2m}\right)^{1/3} n^{2/3}E^{2/3} \,, \tag{A3}$$

which has the same dependence on n and E as in Eq. (2.8), but with a different constant.

APPENDIX B: NORMALIZATION OF WAVE FUNCTIONS

We have

$$\Psi = C[\mathrm{Ai}(Z) + \beta\,\mathrm{Bi}(Z)] = C\bar{\Psi}$$

if we demand

$$\int_0^L |\Psi(x)|^2\,dx = 1 \tag{B1}$$

or

$$1 = \int_{-t_1}^{t_2} |\Psi(Z)|^2\,\frac{dZ}{\alpha_1^{1/3}} \,,$$

where $t_1 = \tilde{\epsilon}/\alpha_1^{1/3}$ and $t_2 = \alpha_1^{1/3}L - t_1$. Integrating by parts,[6] remembering the differential equation, namely,

$$\frac{d^2\Psi}{dZ^2} = Z\Psi(Z) \,,$$

we get

$$C = \alpha_1^{1/6}/D \,, \tag{B2}$$

where

$$D^2 = t_2\bar{\Psi}^2(t_2) + t_1\bar{\Psi}^2(-t_1) - \left(\frac{d\bar{\Psi}}{dZ}(t_2)\right)^2 + \left(\frac{d\bar{\Psi}}{dZ}(-t_1)\right)^2 .$$

Using (2.3), which for $\Psi(Z)$ reads

$$\Psi(t_2) = \Psi(-t_1) = 0 \,,$$

we have

$$D = \left[\left(\frac{d\bar{\Psi}}{dZ}(-t_1)\right)^2 - \left(\frac{d\bar{\Psi}}{dZ}(t_2)\right)^2\right]^{1/2} \,.$$

For case (a) in Sec. II,

$$\frac{d\bar{\Psi}}{dZ}(t_2) \approx -\pi^{-1/2}t_2^{1/4}\exp(-\tfrac{2}{3}t_2^{3/2})$$

[using (2.11)], and for $\alpha_1^{1/3}L \gg 1$ this term is very small and can be neglected. At $-t_1$, $\beta\,\mathrm{Bi}(-t_1)$ is much smaller than $\mathrm{Ai}(-t_1)$, thus $D \simeq d\,\mathrm{Ai}/dZ|_{-t_1}$. For large n, we have (by 10.4.96, 10.4.105 of Ref. 12)

$$D_n = (-1)^{n-1}[\tfrac{3}{8}\pi(4n-1)]^{2/3}$$

and

$C_n \approx \alpha_1^{1/6}/(\frac{3}{2}\pi n)^{2/3}$.

APPENDIX C

The numerical solution of (3.2) was carried out by transforming it (see Eq. 4-J-12, Ref. 22) into a difference equation. We used four crystal lengths, $L = 10d$, $20d$, $60d$, $100d$, divided into M small intervals. Two independent initial-value solutions were constructed for every value of the energy parameter ranging over the interesting region

$$\Psi_1(0) = 0; \quad \Psi_1(1) = 1; \quad \Psi_2(0) = 1; \quad \Psi_2(1) = 0 \ . \quad \text{(C1)}$$

The solutions $\Psi_1(m)$, $\Psi_2(m)$ are calculated from (3.2) and (C1), up to the other end point. Now we have to satisfy the various BC. To satisfy condition (i) is the simplest. We look for those energies for which $\Psi_1(M) = 0$. To satisfy numerically condition (iii) we need to build a function

$$\Psi(n) = \gamma \Psi_1(n) + \beta \Psi_2(n) \quad . \quad \text{(C2)}$$

such that

$$\Psi(0) = \Psi(M), \quad \Psi(1) = \Psi(M+1) \ . \quad \text{(C3)}$$

Inserting (C1) and (C2) in (C3) we get two homogeneous algebraic equations, which have a solution only if the determinant of the coefficients vanishes, i.e.,

$$\begin{vmatrix} \Psi_1(M) & \Psi_2(M) - 1 \\ \Psi_1(M+1) - 1 & \Psi_2(M+1) \end{vmatrix} = 0 \quad . \quad \text{(C4)}$$

Now we use the fact that the Wronskian of (3.2) (which is a Sturm-Liouville type of equation) is a constant. In the discrete case, that is equivalent[23] to

$$\begin{vmatrix} \Psi_1(n) & \Psi_2(n) \\ \Psi_1(n+1) & \Psi_2(n+1) \end{vmatrix} = \text{const} = -1 \ . \quad \text{(C5)}$$

The last result comes from (C1). With (C5) we get from (C4) that in order to fulfill condition (iii) we must have

$$R_c = \Psi_1(M+1) + \Psi_2(M) - 2 = 0 \ . \quad \text{(C6)}$$

We change ϵ until condition (C6) is satisfied. By a similar method we have that condition (ii) is fulfilled if we demand

$$R_b = \Psi_2(M+1) + (u-1)\Psi_2(M) + (1+u)\Psi_1(M+1) + (u^2-1)\Psi_1(M) = 0 \ , \quad \text{(C7)}$$

where $u = \bar{\alpha} h d/\pi$; $h = N\pi/M$ is the numerical increment.

We used a constant value for $\bar{\alpha}$, $\bar{\alpha} d/\pi = 3$. This is equivalent to having a fixed $(V_0 - \epsilon)$ of approximately 11 eV in the above example, and is a slightly different case from that discussed previously. It is analogous if $\epsilon \ll V_0$, and for higher energies similar to increasing the height of the walls. Two values were used for S: $S = 1$ and $S = 5$.

APPENDIX D

The BL theorem states that the distribution of eigenvalues for the frequencies of lattice vibrations changes very slightly with a change in BC. The proof is based on a theorem by Cauchy,[16] from which the following intermediate theorem (T) is obtained in Ref. 16: "If in a finite Hermitian matrix, the elements of r rows and their corresponding columns are modified in any way whatever, provided only that the matrix remains Hermitian, then the number of latent roots which lie in any given interval cannot increase or decrease by more than $2r$." The original proof[16] goes on to show the validity of the above-mentioned BL theorem. We use theorem T in order to show that for the similar case of the electronic energy eigenvalues for a *finite* crystal, with or without external fields, the exact form of the BC has a negligible effect on their distribution. We use the notation for a one-dimensional crystal with a length L in an electric field, but the same treatment applies for the general case of a self-adjoint equation.

We treat a differential equation of the form

$$\hat{\mathcal{H}}\Psi = \frac{d^2\Psi}{dx^2} + W(x)\Psi(x) + \epsilon\Psi(x), \quad 0 \le x \le L \ . \quad \text{(D1)}$$

We assume that (D1) can be transformed into a difference equation. Note the following: (a) A numerical solution of (D1) is always carried out in this way, the range of x being finite. (b) The following arguments do not depend on the number of intervals we divide L into, so this number can be made to tend to infinity. (c) The exact difference scheme is immaterial provided $\hat{\mathcal{H}}$ remains Hermitian. We can, for example, use for the second differential $d^2\Psi/dx^2$, the second difference $(1/h^2)(\Psi_{n+1} + \Psi_{n-1} - 2\Psi_n)$, and get

$$\hat{\mathcal{H}}\Psi = (1/h^2)(\Psi_{n+1} + \Psi_{n-1} - 2\Psi_n) + W(nh)\Psi(nh) = \epsilon\Psi(nh) \ , \quad \text{(D2)}$$

where $1 \le n \le M-1$; $h = L/M$ is the length of the interval. This can be written as

$$\Psi_{n+1} + \Psi_{n-1} + (A_n - \epsilon)\Psi_n = 0 \ . \quad \text{(D3)}$$

We cannot write the equations for $n = 0$, M without knowing the BC. From the operator alone we have a system of $M-1$ equations in $M+1$ unknowns (the Ψ_n's). Adding the BC gives a system of the same number of equations and unknowns, the solution of which is given by finding the latent roots of the appropriate secular equation. Using self-adjoint BC [as, e.g., those we use in this work, namely, the types (i)–(iii), above] does not change the Hermiticity of the secular matrix. Moreover they

can influence at most the two last rows and corresponding two last columns. Thus we can use theorem T to get that the number of energy eigenvalues which lie in any given interval does not change by more than four. As mentioned before, increasing M does not change the argument.

In applying the above for our case, we can restrict the change in the number of eigenvalues even further. First, we show that this change between types (i) and (iii) can be at most one: On using $\Psi_0 = 0$ and $\Psi_M = 0$ we get that the first ($n = 1$) and last ($n = M - 1$) equations will transform into

$$\begin{aligned} &\Psi_2 + (A_1 - \epsilon)\Psi_1 = 0 , \\ &\Psi_{M-2} + (A_{M-1} - \epsilon)\Psi_{M-1} = 0 , \end{aligned} \tag{D4}$$

and we get a set of $M - 1$ homogeneous equations with $M - 1$ unknowns. While using BC type (iii), namely, $\Psi_0 = \Psi_M$, $\Psi_1 = \Psi_{M+1}$, we get from the first equation $\Psi_2 + (A_1 - \epsilon)\Psi_1 + \Psi_M = 0$ and there will be an M equation reading $\Psi_{M-1} + (A_M - \epsilon)\Psi_M + \Psi_1 = 0$. Thus in case (i) the secular matrix is a leading minor of the secular matrix of case (iii). But the change in the number of eigenvalues, in any interval between a matrix and its leading minor, cannot be[16] more than one. Now in case (ii) we get for the equation for $n = 1$

$$\Psi_2 + (A_1 + \rho)\Psi_1 = 0$$

and for the $M - 1$ equation

$$\Psi_{M-2} + (A_{m-1} + \rho')\Psi_{M-1} = 0 ,$$

where $\rho = (1 + \bar{\alpha}h)^{-1}$, $\rho' = 1 - \bar{\alpha}h$. Thus the change between cases (ii) and (i) (using the above theorem) can be at most two.

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