Band Structures of One-Dimensional Crystals with Square-Well Potentials

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The energy band structure for a one-dimensional periodic square-well potential is obtained in terms of the well depth for the whole range of possible ratios of well width to hill width. This model bears a closer resemblance to a real crystal since, as potential depth is varied for a fixed ratio of well width to hill width, the curves bounding distinct bands cross while in the case of a delta-function potential no such crossings occur. The location of these crossings is derived. The number of times that a given pair of boundary curves can cross is considered. For the set of boundary curves that belong to a given ratio of well-to-hill widths, this number is unbounded.

I. INTRODUCTION

THE eigenspectrum of the Schrödinger equation for the motion of an electron in a crystal with a periodic potential is continuous except for certain unallowed regions (band structure). Considerable information about many properties of solids (e.g., electrical conductivity and cohesive energy) can be deduced from the structure of the eigenspectrum. In general, approximate methods have to be applied in solving such problems. In order to estimate the validity of a particular method, one can apply it to a one-dimensional model in which the potential is reasonably similar to that assumed for the three-dimensional case. The determination of the band structure in the one-dimensional case may also be useful in providing some insight into the nature of a real crystal.[1]

Mathematically, one has the problem of finding the allowed and unallowed regions of the solution of the equation

$$d^2\psi/dx^2+[E-V(x)]\psi=0, \tag{1}$$

where E is the total energy and $V(x)$ is a periodic function which in some way possesses properties similar to those of the potential for real crystals. A particularly simple form of $V(x)$ is provided by the function $V_0S(x)$, where V_0 is the depth of the potential well (or height of the potential hill) and $S(x)$ is a periodic function like that shown in Fig. 1 which takes on only the values 0 and 1. In Fig. 1, h is one-half the width of the hill and w is one-half the width of the well.

Equation (1) has been studied in detail for the case where $V(x)$ is sinusoidal, in which case the solutions are Mathieu functions. For $V(x)$ of the form $V_0S(x)$, the allowed and unallowed regions of Eq. (1) have previously been determined for the case[2,3] $h=w$ and for the Kronig-Penney potential.[4,5] For the former case curves of E *vs* V_0 in the interior of a band have also been calculated.[3] We shall here undertake to treat the case of arbitrary w/h,[6] but we shall limit ourselves to curves which bound the zones.

One very important feature of the band structure is the existence of points of contact between different allowed bands (a special type of band crossing). Aside from its general mathematical interest, the question of the distribution of these points of contact deserves attention because of its connection with the problem of surface states, as pointed out by Shockley.[7] The band structures for both the Kronig-Penney and the sinusoidal potential are not qualitatively the same as that of real crystals, since points of contact occur in those of real crystals but not in these models.[5,8] As was shown by Landauer,[9] the band structure in the case of the Kronig-Penney potential is dissimilar to that of real crystals in yet another way. While in the former case, the size of the forbidden regions approaches a constant nonvanishing value as E approaches infinity, in actual crystals if V_0 is kept fixed, the forbidden ranges of E approach zero as E approaches infinity.

The band structure for the case of a finite rectangular well potential, on the other hand, has the proper behavior as E approaches infinity and (as will be shown) has an infinite number of points of contact whenever $h\neq 0$. However, in order to carry out a

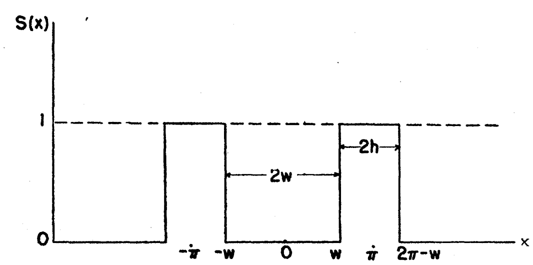

FIG. 1. The function $S(x)$ for a potential function of period 2π.

[1] E. Fues and H. Statz, Z. Naturforsch. **7a**, 2 (1952).
[2] M. T. O. Strutt, *Lamésche-Mathieusche und Verwandte Funktionen* (Verlag. Julius Springer, Berlin, 1932), p. 39. The numbers Strutt uses to label the E axis in his Fig. 4 are too large by a factor of 4.
[3] H. Statz, Z. Naturforsch. **5a**, 534 (1950).
[4] R. Del. Kronig and W. G. Penney, Proc. Roy. Soc. (London) **A130**, 499 (1930).
[5] D. S. Saxon and R. A. Hutner, Philips Research Repts. 4, 81 (1949).
[6] See also G. Allen and Rolf W. Landauer, Bull. Am. Phys. Soc. **28**, No. 3, 47 (1953).
[7] W. Shockley, Phys. Rev. **56**, 317 (1939).
[8] J. J. Stoker, *Nonlinear Vibrations* (Interscience Publishers, Inc., New York, 1950), Chap. VI.
[9] Rolf W. Landauer, thesis, Harvard University, 1949 (unpublished).

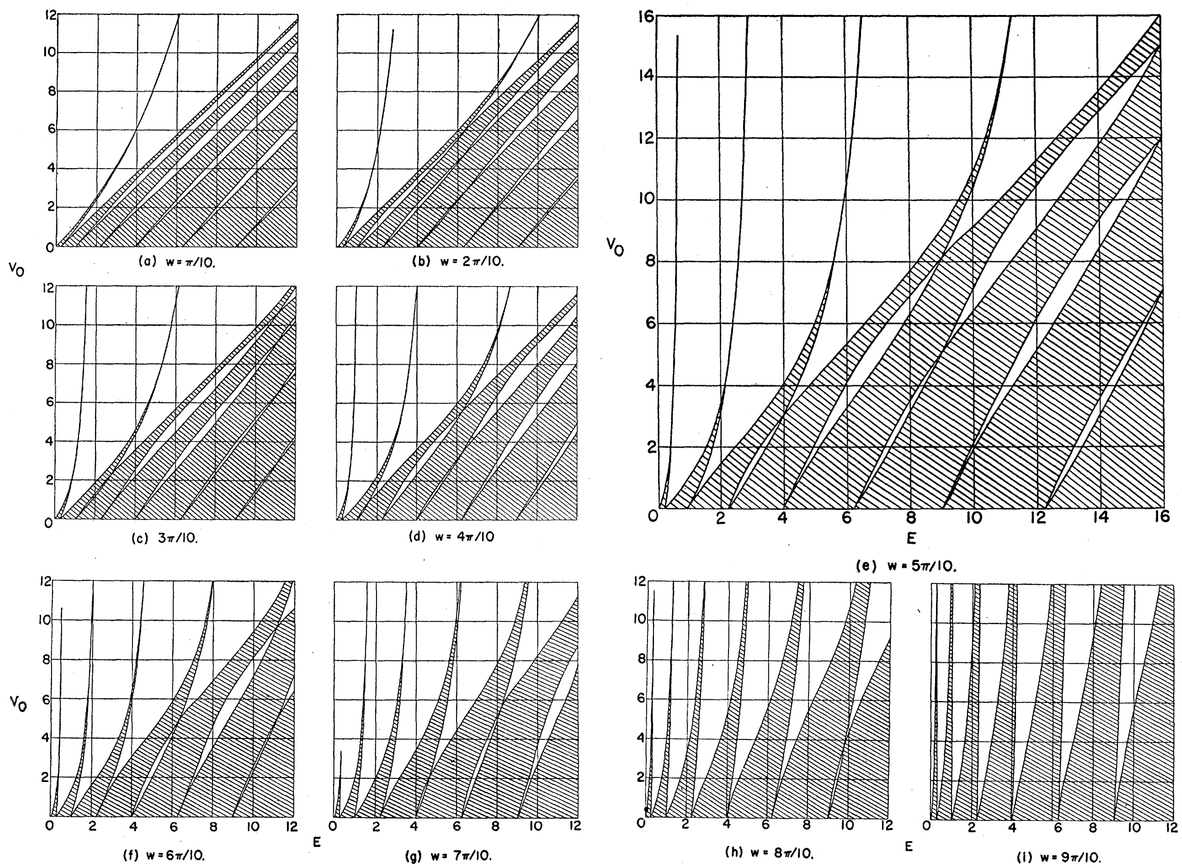

FIG. 2. Band structure as a function of energy and well depth. In (e), note the recrossing of the boundary curves which share the exceptional point $E=6.25$ on the E axis.

one-dimensional calculation analogous to the usual three-dimensional one, it is necessary to find the band structure for a whole range of values of w/h. This corresponds to the usual procedure of varying the lattice spacing in order to determine the most stable configuration of a crystal. For this reason, the restriction $w=h$ is objectionable.

II. THE EIGENSPECTRUM

Without loss of generality we shall confine ourselves to the case where $S(x)$ has the period 2π. Then the bounded solutions of Eq. (1) can always be represented as combinations of functions having the property

$$\psi(x+2n\pi)=e^{ink}\psi(x), \tag{2}$$

k being a real number and n an integer.[10] The value of k can be determined from E and V_0 when $E>V_0$ by the relation,[11]

$$\cos(2u)\cos(2v)-\left[\frac{w^2u^2+(\pi-w)^2v^2}{2(\pi-w)wuv}\right]\sin(2u)\sin(2v)=\cos(nk), \tag{3}$$

where $u=(\pi-w)(E-V_0)^{\frac{1}{2}}$, and $v=wE^{\frac{1}{2}}$.

Equation (3) is valid for all the points (E, V_0) for which $E>V_0$ and for which Eq. (1) has bounded solutions. At the boundary curves, however, $\cos(nk)$ assumes an extreme value, that is ±1. In these cases, Eq. (3) is factorable and the equations for the boundary curves may be written

$$u\tan u=-[(\pi-w)/w]v\tan v, \tag{4a}$$

$$u\cot u=-[(\pi-w)/w]v\cot v, \tag{4b}$$

$$u\cot u=[(\pi-w)/w]v\tan v, \tag{4c}$$

$$u\tan u=[(\pi-w)/w]v\cot v, \tag{4d}$$

where Eqs. (4a) and (4b) are the factors of Eq. (3) when $\cos(nk)=+1$, and Eqs. (4c) and (4d) are the factors when $\cos(nk)=-1$. An equation similar to Eq. (3) results for $E<V_0$, and the equations for the boundary curves are then identical with Eqs. (4) with u replaced

[10] F. Block, Z. Physik **52**, 555 (1928).
[11] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 282.

by iu so that hyperbolic functions replace the trigonometric ones.

Equations (4) and the corresponding set for $E<V_0$ were used to obtain the plots of Figs. 2(a) to 2(i). In these graphs the shaded regions represent allowed regions, and the white ones, the unallowed regions. For each interior point of the shaded (allowed) regions, Eq. (1) has two linearly independent bounded solutions. Along the boundary curves separating allowed from unallowed regions, Eq. (1) has, in general, a unique bounded solution. However, there exists a discrete set of exceptional points for each of which Eq. (1) has two linearly independent solutions corresponding to two different boundary curves which, therefore, have such points in common. In the standard treatment of Hill's equation, it is shown that any two such curves having one or more points in common in the finite plane must both bound the same unallowed region, so that the widths of the allowed bands there never vanish. Those exceptional points which occur in the interior in the finite part of the $E-V_0$ plane correspond to a crossing of the boundary curves. In addition to these, there are junctions in which pairs of curves meet on the E axis and at infinity. In the latter case, the curves meeting at infinity both bound the same allowed band.

III. LOCATION OF THE EXCEPTIONAL POINTS

A. Crossings

The exact location of the crossings may be found by considering Eqs. (4). Any values of u and v, such that any two of these equations are satisfied simultaneously, determine a crossing. The crossings are found to occur at the points

$$\begin{pmatrix} E=n^2\pi^2/4w^2, \\ V_0=n^2\pi^2/4w^2-[m^2\pi^2/4(\pi-w)^2] \end{pmatrix}, \quad V_0\neq 0, \quad n\neq 0, \tag{5}$$

where n and m are integers.

A similar consideration of the equations analogous to Eqs. (4), when $E<V_0$, shows that no pair of these equations can be satisfied simultaneously for finite u's and v's. Hence, we conclude that crossings of the type previously described can occur only when $E>V_0$, and the location of these is given by Eq. (5).

B. Junctions on the E Axis

When $V_0=0$, Eq. (1) becomes

$$d^2\psi/dx^2+E\psi=0,$$

which has bounded solutions for all positive values of E. Hence, there are no forbidden regions along the E axis and each boundary curve ends in an exceptional point. The location of these junctions is readily found from Eq. (4). They are at the points

$$(E=n^2/4,\ V_0=0), \quad n\neq 0, \tag{6}$$

where n is an integer.

C. Asymptotic Junctions

Although no crossings occur in the finite plane when $E<V_0$, it may be shown that pairs of boundary curves share the vertical asymptotes

$$E_\infty=n^2\pi^2/4w^2, \quad n=1, 2, 3, \cdots. \tag{7}$$

These junctions are all between pairs of curves bounding allowed regions.

IV. THE NUMBER OF EXCEPTIONAL POINTS

The number of junctions is clearly equal to the number of boundary curves. We shall now establish that, given any prescribed integer N, there exists for any value of w a set of boundary curves which crosses more than N times.

We first find the number of crossings in a right triangle bounded by the E axis, the line $E=V_0$, and a vertical line $E=n_{\max}{}^2\pi^2/4\pi^2$, where $n_{\max}$ is an integer. Every crossing within the triangle is located at the intersection of a vertical line, $E=n^2\pi^2/4w^2$, and a line of slope one, $V_0=E-m^2\pi^2/4(\pi-w)^2$. The number of crossings is thus equal to the number of such intersections of diagonal lines with vertical lines. There will obviously be $n_{\max}$ such vertical lines if we include the boundary of the triangle as one of the lines. For large $n_{\max}$, to a good approximation, the number of crossings ν will be given by

$$\nu=[(\pi-w)/2w]n_{\max}{}^2. \tag{8}$$

We next find the number of pairs of boundary curves among which these double points are distributed. We know that a pair of boundary lines passes through the base of the triangle at the points $E=n^2/4$. Therefore, there are at most $n_{\max}$ such boundary pairs. Since (as can be shown) the slope of these curves is always positive, no boundary curve which starts at $V_0=0$ outside the triangle will enter it. Thus, the ratio of the number of double points to the number of boundary curves is directly proportional to $n_{\max}$ for large $n_{\max}$.

Now if there are p double points to be distributed among q boundary pairs, there must be at least one boundary pair having at least p/q double points along it. Since p/q is a linear function of $n_{\max}$, a pair of boundary curves can be found with any given number of crossings.

Note that the preceding discussion does not exclude the possibility that between two pairs of boundary curves having a large number of crossings there are sandwiched pairs of boundary curves having a smaller number or, perhaps, no crossings at all.

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