PHYSICAL REVIEW VOLUME 180, NUMBER 3 15 APRIL 1969

Saxon-Hutner Theorem for One-Dimensional General Alloys

B. Y. TONG*
Physics Department, University of Western Ontario, London, Ontario

AND

S. Y. TONG
Physics Department, University of California, Irvine, California 92664

(Received 12 November 1968)

A proof of the conjecture made in a previous paper concerning a sufficient condition of the Saxon-Hutner theorem for random binary alloys of symmetric potentials is given. Sufficient conditions of the Saxon-Hutner theorem for general alloys of arbitrary number of different constituent potentials are established for both the symmetric and nonsymmetric cases. A numerical calculation of the central-square-well-potential alloys is also presented.

I. INTRODUCTION

In a previous paper, hereafter referred to as I,[1] we have studied in some detail the electronic spectra of binary alloys in relation to the spectra of the alloying constituents. A phase-transfer method was used in which the transfer matrix

$$\mathbf{M}=\begin{pmatrix} u^* & v \\ v^* & u \end{pmatrix} \tag{1}$$

plays the fundamental role. It transforms the wave function $\Psi=c_1e^{-ik\cdot r}+c_2e^{ik\cdot r}$ from one cell to the next:

$$\begin{pmatrix} c_1' \\ c_2' \end{pmatrix}=\mathbf{M}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}. \tag{2}$$

For binary alloys of symmetric potentials A and B, the electronic structure was studied in terms of the parameter

$$\Delta_{BA}=\eta_A\eta_B-\xi_A\xi_B\,, \tag{3}$$

where we have defined

$$u=\omega+i\xi \tag{4a}$$

and

$$v=\nu+i\eta\,. \tag{4b}$$

For symmetric potentials, $\nu=0$ [Eq. (I10)]. It was also shown that the parameter Δ_{BA} can be expressed in terms of the scattering phase shifts. Thus, for symmetric localized potentials,

$$\begin{aligned} \omega&=\frac{\cos(\delta_+ +\delta_-)}{\cos(\delta_+ -\delta_-)}\,,\\ \xi&=\frac{\sin(\delta_+ +\delta_-)}{\cos(\delta_+ -\delta_-)}\,,\\ \nu&=0,\quad \eta=-\tan(\delta_+ -\delta_-)\,, \end{aligned} \tag{5}$$

where δ_+ and δ_- are the even and odd phase shifts defined in I. We characterize the given potentials by their scattering phase shifts. This formulation gives us a clear association between the given potentials and its resulting electronic spectra of the alloys.

One of the main questions studied in I was the conditions under which the Saxon-Hutner theorem is valid. The theorem states that a level forbidden in an infinite one-dimensional lattice formed of pure type-A potentials and forbidden in that formed of pure type-B potentials is also forbidden in any arbitrary alloy of A and B. Several sufficient conditions were found under which the above theorem is valid. One particular condition, which is of special interest to us here, states that the Saxon-Hutner theorem in binary alloys of symmetric potentials is valid for an alloy of the type A^r-B^s (i.e., a periodic alloy of r type-A potentials followed by s type-B potentials, where r and s are arbitrary integers) if

$$\operatorname{sgn}(\omega_A\omega_B)=\operatorname{sgn}(\Delta_{BA})\,. \tag{6}$$

From Eq. (5), we see that

$$\omega^2-1=\eta^2-\xi^2\,, \tag{7}$$

and for forbidden levels we have $|\omega|>1$, giving $|\eta|>|\xi|$. Hence we can rewrite the equality in (6) as

$$\operatorname{sgn}(\omega_A\omega_B)=\operatorname{sgn}(\eta_A\eta_B) \tag{6$'$}$$

or

$$\omega_A\omega_B\eta_A\eta_B>0\,. \tag{8}$$

The proof was extended to the fourth-order type (i.e., $A^{r_1}B^{s_1}\cdots A^{r_4}B^{s_4}$) and several other special situations. It was conjectured that the same condition (6) is sufficient to ensure the validity of the Saxon-Hutner theorem for an infinitely random binary alloy of symmetric potentials A and B: $A^{r_0}B^{s_0}A^{r_1}B^{s_1}\cdots A^{r_\infty}B^{s_\infty}$, with arbitrary integer superscripts r_i and s_i. We have shown that this condition includes the Luttinger[2] central δ-potential substitutional alloy as a special

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* Supported by the National Research Council of Canada.

[1] B. Y. Tong, Phys. Rev. **175**, 710 (1968).

[2] J. M. Luttinger, Philips Res. Rept. **6**, 303 (1951).

case. A similar condition was observed by Dworin[3] in random alloys. The condition (6) is of particular interest because it does not refer to a specific energy value. The energy ranges satisfying the inequality given in Eq. (8), in general, lead to the formation of energy gaps in the alloys.

In Sec. II we present a proof of the conjecture made in I concerning the sufficient condition [Eq. (6)] of the Saxon-Hutner theorem for infinitely random binary alloys of symmetric potentials. We then extend our consideration to include general alloys of arbitrary numbers of different constitutent symmetric potentials. Sufficient conditions for nonsymmetric potentials in general alloys are also established. The Hori-Matsuda[4] method of the Möbius transformation is used. Numerical calculations of the central-square-well-potential alloys are given in Sec. III. The purpose of the latter analysis is twofold: We want to illustrate how to handle the phase shifts introduced in I in practical calculation, and the result of the square-well calculations serves to explain why Landauer and Helland[5] thought that the Saxon-Hutner conjecture is not valid for such potentials. Concluding remarks are given in Sec. IV.

II. HORI-MATSUDA METHOD AND SAXON-HUTNER THEOREM

Hori and Matsuda[3] showed that the properties of the transfer matrix M can be studied in terms of a Möbius transformation (or linear fractional transformation) in the theory of complex variables.[6] Let us denote

$$z=c_1/c_2\,, \quad z'=c_1'/c_2'\,. \tag{9}$$

With this notation, Eq. (2) becomes

$$z'=(u^*z+v)/(v^*z+u)\,. \tag{10}$$

The determinant $|u|^2-|v|^2=1$. This transformation induces a one-to-one conformal mapping of the complex plane into itself. A point z in the complex plane mapped into itself is called a "fixed point." In general, the Möbius transformation has two fixed points, z_1 and z_2. In our problem here, Eq. (10) gives the two fixed points at

$$z_{1,2}=(1/v^*)\{\tfrac{1}{2}(u^*-u)\pm[(\tfrac{1}{2}(u^*+u))^2-1]^{1/2}\}\,. \tag{11}$$

Consider a chain of pure type-A potentials. In passing from left to right, a wave function is multiplied by the transfer matrix $\mathbf{M}$ once every time it passes through a cell. In terms of the Möbius transformation, it means that z, the ratio of c_1 to c_2 of a wave function, is mapped n times when the wave function is transferred through n cells. The problem of curves traced out by such successive Möbius transformations having two fixed points is one of kinematics.[6] The motion, in general, can be classified into two groups.

(*a*) *Two coincident fixed points at* z_0. Equation (10) can be put into the form

$$(z'-z_0)^{-1}=(z-z_0)^{-1}+v^*\,, \tag{12}$$

and the motion is called parabolic [Fig. 1(a)]. We see from Eq. (11) that this corresponds to the band edge: $|\omega|=1$.

(*b*) *Two distinct fixed points at* z_1 *and* z_2. Equation (10) can now be put into the form

$$\frac{z'-z_1}{z'-z_2}=G\frac{z-z_1}{z-z_2}\,, \tag{13}$$

where

$$G=(v^*z_1+u)/(v^*z_2+u)\,. \tag{14}$$

In a general Möbius transformation, G is complex and the motion is called loxodromic. In particular, if G is real and not equal to unity, the motion is called hyperbolic; and if G is complex with $|G|=1$, the motion is called elliptic. Using Eqs. (11) and (14), we find that

$$G=\frac{\omega+(\omega^2-1)^{1/2}}{\omega-(\omega^2-1)^{1/2}}\,. \tag{15}$$

This corresponds to hyperbolic motion when $|\omega|>1$ [Fig. 1(b)] and elliptic motion when $|\omega|<1$ [Fig. 1(c)]. Here we do not need to consider the general loxodromic motion. We notice that forbidden levels in a pure lattice ($|\omega|>1$) correspond to hyperbolic motion in which all lines never close upon themselves. Physically this means that a wave function after transferring through the cells can never satisfy the propagation condition of a periodic lattice. In hyperbolic motion, all lines start from one fixed point and end at the other. Thus, the two fixed points have the properties of a source z_+ and a sink z_-. From Eq. (11), we see that the two fixed points of the hyperbolic motion are at

$$z_{1,2}=\frac{[\eta\xi\pm\nu(\omega^2-1)^{1/2}]+i[-\xi\nu\pm\eta(\omega^2-1)^{1/2}]}{\nu^2+\eta^2} \tag{16}$$

$$=e^{i\phi_{1,2}}\,, \tag{17}$$

where

$$\tan\phi_{1,2}=\frac{\xi\nu\pm\eta(\omega^2-1)^{1/2}}{-\eta\xi\pm\nu(\omega^2-1)^{1/2}}\,. \tag{18}$$

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[3] L. Dworin, Phys. Rev. **138**, A1121 (1965). As was shown in Ref. 13 of I, the Dworin conditions for a forbidden level in the binary alloy are

$$|\omega_A{}^2+[\omega_A\omega_B/(\Delta-\mu_{BA})](\omega_A{}^2-1)|\geqslant 2$$

and

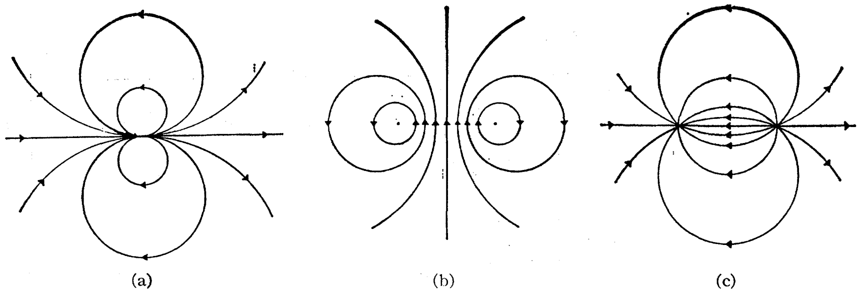
$$|\omega_B+[\omega_A/(\Delta_{BA}-\mu_{BA})](\omega_A{}^2-1)|\geqslant 2,$$

with $|\omega_A|\geqslant 1$ and $|\omega_B|\geqslant 1$. Δ_{BA} and μ_{BA} are defined in I. When $|\omega_A|\geqslant 1$ and $|\omega_B|\geqslant 1$ simultaneously, it is easily checked that $\operatorname{sgn}(\Delta_{BA}-\mu_{BA})=\operatorname{sgn}(\Delta_{BA}+\mu_{BA})=\operatorname{sgn}(\Delta_{BA})$. Now when $\operatorname{sgn}(\omega_A\omega_B)=\operatorname{sgn}(\Delta_{BA})$, we see that the two terms in each of the above conditions add, and only when the magnitudes add is it more likely to produce a magnitude greater than 2. $\operatorname{sgn}(\omega_A\omega_B)=\operatorname{sgn}(\Delta_{BA})$ is our sufficient condition (6).

[4] Jun-ichi Hori and Hirotssuju Matsuda, Progr. Theoret. Phys. (Kyoto) **32**, 183 (1964).

[5] R. Landauer and L. C. Hellund, J. Chem. Phys. **22**, 1655 (1954).

[6] See, e.g., Einar Hille, *Analytic Function Theory* (Blaisdell Publishing Co., Waltham, Mass., 1959), Vol. 1, p. 53.



(a) (b) (c)

FIG. 1. Lines of motion of the Möbius transformation in the complex plane for (a) the parabolic, (b) the elliptic, and (c) the hyperbolic cases.

Thus, we see that the two fixed points always lie on the unit circle for forbidden levels. When the alloying potentials are symmetric, $\nu=0$. The two fixed points subtend equal angles $|\phi|$ about the real axis:

$$\phi=\phi_1=-\phi_2=\tan^{-1}[(1-x^2)^{1/2}/x], \tag{19}$$

where

$$|x|=|\xi/\eta|<1.$$

Now consider an alloy formed of two different symmetric potentials, types A and B. Let us look at energy levels that are forbidden in both type-A and type-B potentials. There will be two sets of hyperbolic motion curves corresponding to A and B in the complex plane, each set having two fixed points lying on the unit circle. A transfer of the wave function through a type-A potential cell corresponds to a motion in the complex plane following a section of the hyperbolic motion curve of set A. When the wave function is transferred through a type-B potential cell, the corresponding motion in the complex plane is by following the flow lines of set B. If the path traced out in this way never closes upon itself we have a forbidden energy level in the alloy. It is clear that a sufficient condition for this to be true is that there will be no source (or sink) in between two sinks (or sources). In other words, when the region occupied by the sources and that by the sinks do not overlap, the level is forbidden in a random alloy. This is the Hori-Matsuda theorem.[4]

We shall now prove that the sufficient condition we gave in Eq. (8) [or in Eq. (6)] does satisfy the Hori-Matsuda requirement that the sources and sinks do not mix in the case of an infinitely random binary alloy of symmetric potentials: $A^{r_0}B^{s_0}A^{r_1}B^{s_1}\cdots A^{r_\infty}B^{s_\infty}$. We shall then modify our condition given in Eq. (8) so that it becomes a sufficient condition under which the Saxon-Hutner theorem is valid for a general alloy of arbitrary numbers of different constituent symmetric potentials. Finally, we shall establish a sufficient condition for general alloys in the case of nonsymmetric potentials.

A. Infinitely Random Binary Alloys of Symmetric Potentials

For a binary alloy of symmetric potentials there are four fixed points, all of which lie on the unit circle. Sources and sinks are symmetric about the real axis. The positions of the fixed points are given in Eq. (11). (We are concerned here only with the forbidden levels and hence the hyperbolic case.) A simple way to find out whether a fixed point is a source or a sink is to consider the direction of flow at an arbitrary point in the z plane. The simplest point to consider is at $z=0$. At this point, the Möbius transformation in Eq. (10) gives

$$z'=(\xi\eta+i\omega\eta)/(\omega^2+\xi^2). \tag{20}$$

The direction of flow is upwards (i.e., z_- above the real axis) or downwards (i.e., z_- below the real axis) according to whether $\omega\eta>0$ or $\omega\eta<0$. Equation (20) shows that both sources will be on one side of the real axis and the sinks on the other side if

$$\operatorname{sgn}(\omega_A\eta_A)=\operatorname{sgn}(\omega_B\eta_B). \tag{21}$$

This is exactly the condition given in Eq. (8). Thus, this condition is sufficient for the validity of the Saxon-Hutner theorem in an infinitely random binary alloy of symmetric potentials.

B. Alloys of Arbitrary Number of Symmetric Potentials

It is now trivial to extend the condition to alloys of any number of different symmetric potentials A, B, C, $\cdots$. In general, for n different constituents, there are $2n$ number of fixed points. Since we are always concerned with levels that are forbidden in each of the pure lattices, these fixed points all lie on the unit circle and each pair is symmetric about the real axis. The n sets of flow-line curves are all hyperbolic. As long as all the sources lie on one side of the real axis and all the sinks on the other side, no path can close upon itself. The corresponding level in the alloy is forbidden. Thus, the modified sufficient condition for the validity of the Saxon-Hutner theorem in arbitrary alloys of symmetric potentials A, B, C, $\cdots$, is

$$\operatorname{sgn}(\omega_A\eta_A)=\operatorname{sgn}(\omega_B\eta_B)=\operatorname{sgn}(\omega_C\eta_C)=\cdots. \tag{22}$$

In terms of phase shifts [see Eq. (5)], this condition takes the form

$$\begin{aligned}&\operatorname{sgn}[\cos(\alpha_+ + \alpha_-)\sin(\alpha_+ - \alpha_-)]\\&\quad=\operatorname{sgn}[\cos(\beta_+ + \beta_-)\sin(\beta_+ - \beta_-)]\\&\quad=\operatorname{sgn}[\cos(\gamma_+ + \gamma_-)\sin(\gamma_+ - \gamma_-)]\\&\quad=\cdots,\end{aligned} \tag{23}$$

where $\alpha_\pm$, $\beta_\pm$, $\gamma_\pm$, $\cdots$, are the even (odd) phase shifts of the symmetric potentials A, B, C, $\cdots$, respectively.

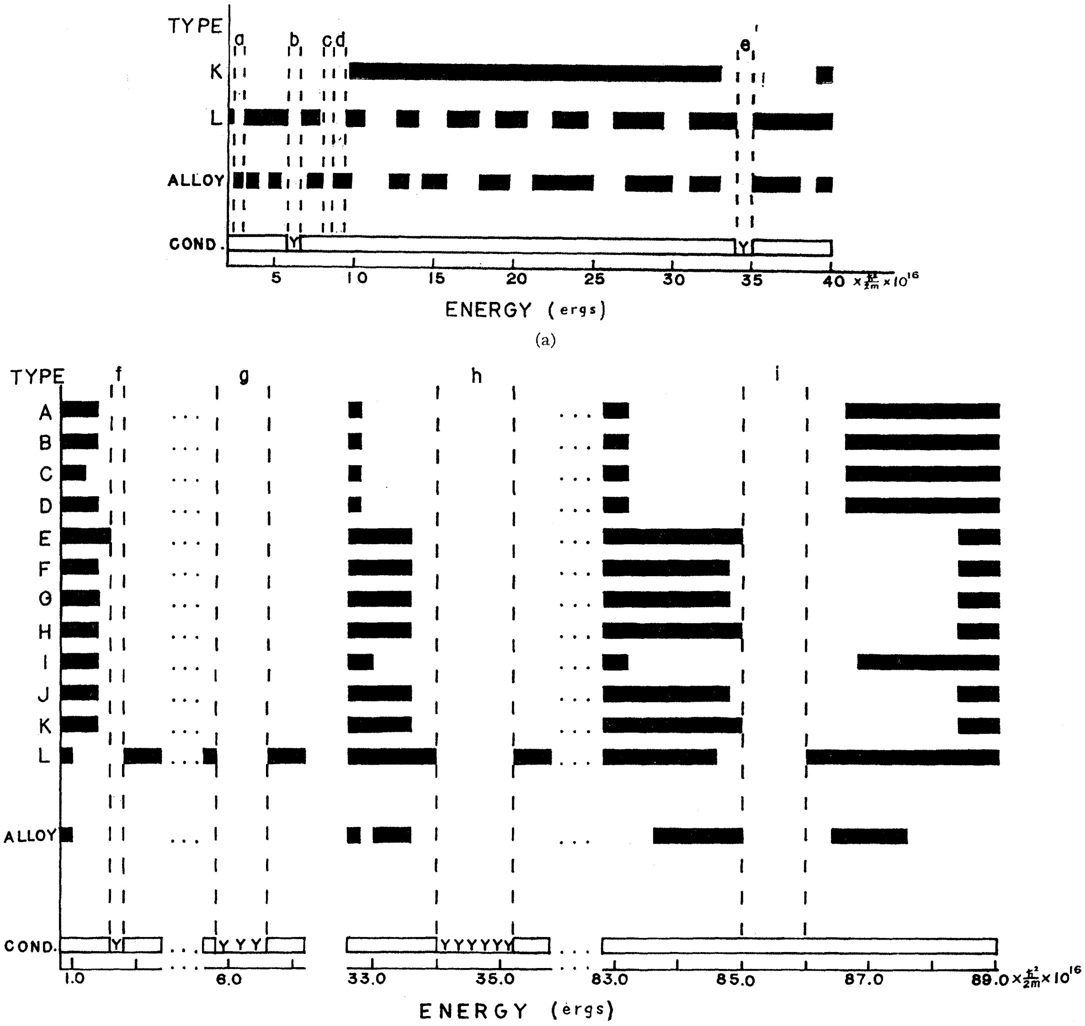


FIG. 2. (a) Energy spectrum of the alloy *KL* and those of its constituents; (b) energy spectrum of the alloy $ABCDEFG^2H^3IJKL$ and those of its constituents. The specification of the constituent symmetric square-well potentials is listed in Table I. Regions in which the condition of Eq. (23) is satisfied are marked by *Y*.

C. Alloys of General Nonsymmetric Potentials

When the potentials of the constituents are nonsymmetric, ν is nonzero. In order to impose sufficient conditions for the Saxon-Hutner theorem, a single parameter is no longer sufficient to characterize the situation. We need two parameters.

Using the Hori-Matsuda theorem, it is not difficult to write down the required sufficient condition. For example, as long as the sources and sinks of the constituent potentials lie on different sides of the real axis, the level is forbidden. From Eq. (17), we see that if we require each of the potential A, B, C, $\cdots$, to satisfy the relation

$$|\eta_i(\omega_i^2-1)^{1/2}|>|\xi_i\nu_i|\,, \tag{24}$$

where $i=A$, B, C, $\cdots$, the sink and the source of each potential lie on different sides of the real axis although they are no longer symmetric about it. Again the identity of sources or sinks can be found by examining the flow direction at $z=0$. All sources are on one side and the sinks on the other side of the real axis if

$$\begin{aligned}&\operatorname{sgn}(\eta_A\omega_A-\xi_A\nu_A)\\&\quad=\operatorname{sgn}(\eta_B\omega_B-\xi_B\nu_B)\\&\quad=\operatorname{sgn}(\eta_C\omega_C-\xi_C\nu_C)\\&\quad=\cdots.\end{aligned} \tag{25}$$

Note that for symmetric potentials $\nu_i=0$, and this reduces to Eq. (22). Together, Eqs. (24) and (25) form a sufficient condition for the validity of the Saxon-Hutner theorem in alloys with random nonsymmetric constituent potentials.

III. CALCULATIONS FOR THE SYMMETRIC SQUARE-WELL POTENTIALS

Here we shall illustrate, by direct computation, the statements made concerning Eqs. (22) and (23).

Symmetric square-well potentials are chosen for this purpose.

Let us consider a pure lattice of symmetric square wells having width a and depth V in a cell of dimension b. The definitions of r and t in Eqs. (I15)–(I56) differ from those of Kahn[7] by a phase change across the cell, namely,

$$r=e^{-i\phi}r_{\mathrm{Kahn}}=\tfrac{1}{2}e^{-i\phi}[\exp(2i\bar{\delta}_{+})-\exp(2i\bar{\delta}_{-})],$$
$$t=e^{-i\phi}t_{\mathrm{Kahn}}=\tfrac{1}{2}e^{-i\phi}[\exp(2i\bar{\delta}_{+})+\exp(2i\bar{\delta}_{-})], \quad (26)$$
$$\phi=E^{1/2}b.$$

Our phase shift δ_+ and δ_- are related to the usual definition of scattering phase shifts by $\delta_+=\bar{\delta}_+-\frac{1}{2}\phi$, $\delta_-=\bar{\delta}_--\frac{1}{2}\phi$. For square-well potentials, $\bar{\delta}_\pm$ are given by[7]

$$\bar{\delta}_{+}=\tan^{-1}[(k'/k)\tan\tfrac{1}{2}k'a]-\tfrac{1}{2}ka,$$
$$\bar{\delta}_{-}=\tan^{-1}[(k/k')\tan\tfrac{1}{2}k'a]-\tfrac{1}{2}ka, \quad (27)$$

where $k=E^{1/2}$ and $k'=(E+V)^{1/2}$. Substituting the values of δ_+ and δ_- for α_+ and α_- in Eq. (23) and doing the same for the other constituents, we can immediately see what energy ranges satisfy the condition given in Eq. (23).

In Fig. 2(a), the energy spectrum of a type-*KL* binary alloy is plotted together with the spectra of its two constituents. Similarly, in Fig. 2(b) the spectrum of an example alloy formed from 12 different symmetric square wells arranged periodically in the type $ABCDEFG^2H^3IJKL$ is presented alongside with the spectra of the individual constituents. The specifications of the cell potentials are listed in Table I. Note that in the energy regions marked *b* and *e* [Fig. 2(a)] and *f*, *g*, and *h* [Fig. 2(b)], where the condition [Eq. (23)] is satisfied, the alloys *AB* and $ABCDEFG^2H^3IJKL$ have energy gaps. This verifies that the condition [Eq. (23)] is indeed sufficient to guarantee the validity of the Saxon-Hutner theorem.

That the condition [Eq. (23)] is sufficient but not necessary can be seen from region *c* [Fig. 2(a)] and *i* [Fig. 2(b)]. In regions *a* and *d* [Fig. 2(a)], the individual constituents have forbidden energy gaps but the resulting alloy *AB* does not have such gaps. In these regions the condition [Eq. (23)] is not satisfied. This illustrates that the Saxon-Hutner conjecture in its original form is not valid in general for square-well potentials, as observed by Landauer and Hellund.[5] Only in regions where the condition [Eq. (23)] is satisfied we can be sure of the validity of the Saxon-Hutner theorem.

TABLE I. Specification of the symmetric square-well cell potentials.

Type	Depth (V) (erg)	Square-well width (a) (10^{-8} cm)	Cell size (b) (10^{-8} cm)
A	20.0	0.200	1.00
B	19.8	0.200	1.00
C	20.0	0.202	1.00
D	19.8	0.202	1.00
E	19.8	0.200	0.99
F	20.0	0.202	0.99
G	20.2	0.200	0.99
H	20.0	0.199	0.99
I	19.8	0.198	1.00
J	20.2	0.198	0.99
K	20.0	0.200	0.99
L	100.0	4.00	10.00

IV. REMARKS

From our one-dimensional alloy studies in I and here, we can make the following remarks about real alloys and amorphous material.

(a) In alloying different constituents, we do not expect that all the characteristic electronic spectrum structures of the individuals are retained in the spectrum of the alloy. We do not expect every energy gap or level common to all the individual constituents to remain in the spectrum of the alloy.

(b) On the other hand, we do expect that some of the individual characteristics are left in the alloy. Some of these retained characteristics may depend on the particular order in which the constituent atoms are arranged. These structure-dependent gaps or levels are more pronounced if the alloying atoms are arranged periodically to form a superlattice.

(c) In addition to these structure-dependent gaps and levels, there exists structure-independent characteristics which remain in the process of alloying. These gaps or levels will not be washed out even in the infinitely random arrangement of the constituents, and will keep the memory of the characteristics of each individual constituent. It is probably safe to say that the forbidden gaps are remembered better than the allowed levels.

ACKNOWLEDGMENTS

We wish to thank Professor J. Hori for making his papers available to us and to Professor W. Kohn and Professor A. A. Maradudin for their interest in this work.

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[7] A. H. Kahn, Am. J. Phys. **29**, 77 (1961).