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Random superstructures

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Predictions of the densities of states are given for various forms of controlled random disorder in artificial multilayered materials or superstructures.

I. INTRODUCTION

With the development of techniques[1] for fabricating artificial, multilayered, periodic materials, it is possible to study controlled randomness and its effects on electronic states of matter. A hint of the suitability of such superstructured materials for randomness studies was contained in the early work of Esaki and Tsu,[2] but since then the greatest experimental effort has been to remove randomness from superstructures and to make the interfaces between layers abrupt and atomically smooth.

Superstructures with two types of randomness can be grown: randomly varying layer thicknesses and random layer compositions. Both metallic and semiconductor superstructures have been grown, and the ideas of this paper will be applicable to either; however, for definiteness we confine our attention to superstructures composed of layered semiconductors GaAs-$Al_xGa_{1-x}As$, where the random variables are the layer thicknesses d and alloy compositions x. We envision that the stochastic variables d and x are determined by a random number generator during the superstructure growth process and that these quantities are preserved for the analyses of data taken from the superstructured sample.

The resulting disorder is controlled, finite in extent, and essentially one dimensional. Its controlled nature is a valuable aid to understanding random systems, because few such systems have been fabricated before. Moreover, controlled-disorder superlattices offer the possibility of studying heretofore unimagined combinations of order and disorder, such as periodically stacked alternating ordered and disordered arrays. The finiteness of the artificially produced disorder offers opportunities to directly determine the extent of localization of states and to study the impending onset of Anderson localization[3] as a function of increasing size. One dimensional random systems are comparatively well understood theoretically; numerous models have been solved exactly and even more have been thoroughly studied.

For electronic states in semiconductor superstructures three theoretical regimes present themselves: the regime of localized deep-trap-like states,[4] the mixed regime of localized and extended states, and the regime of extended states described by effective-mass theory.[5] The most interesting is the one-band effective-mass theory of carrier motion, which we shall consider. This regime has two subregimes: the quantum well limit[6] in which the effective-mass electron's de Broglie wavelength is comparable with or larger than typical superstructure dimensions, and the classical limit in which the electronic spectrum is characteristic of a classical particle colliding with barriers. In this paper we shall restrict our attention to the quantum well limit.[7,8]

The standard theoretical questions to be answered by any theory of disorder are as follows: (i) What is the ensemble-averaged density of states for the random system? (ii) Are the band gaps of the ordered structure preserved in spite of the disorder or annihilated by it? (iii) Can selected types of disorder *introduce* gaps into a spectrum that would otherwise be continuous? (iv) To what extent does the disorder produce localized states, is diffusion possible, and what is the transmission coefficient for an electron in a random superstructure? (v) What are the effects of "many body" interactions between electrons confined to adjacent layers and can they produce one-dimensional

quasi-phase-transitions?[9] Here we shall present answers to the first three questions; subsequent work will deal with localization and phase transitions.

In this paper we consider a random superlattice in the quantum-well limit, show how its density of states can be evaluated, and illustrate how the band gaps depend on the disorder.

II. MODEL

Since the primary purpose of this paper is to illustrate the physics of random superstructures, we take the simplest possible model. For a periodic superlattice in the z direction (Fig. 1), the Hamiltonian is taken to be

$$H=\frac{p_x^2+p_y^2}{2m}+H_z \ , \tag{1}$$

where

$$H_z=\sum_{n=1}^{N}[\,W_n|n\rangle\langle n|+V_n(|n\rangle\langle n+1| + |n+1\rangle\langle n|)] \ , \tag{2}$$

and the (isotropic) one-band effective-mass approximation is assumed valid for the electronic motion in the x and y directions. The energy W_n is the energy of the single state[10] bound in the nth quantum well, and is taken to be zero for the periodic superlattice. The tunneling matrix element V_n from the nth to the $(n+1)$st well can be evaluated using the tunneling Hamiltonian formalism of Bardeen,[11] Harrison,[12] Cohen *et al.*,[13] and Prange[14] (see the Appendix), and is a constant for the periodic superlattice of Fig. 2.

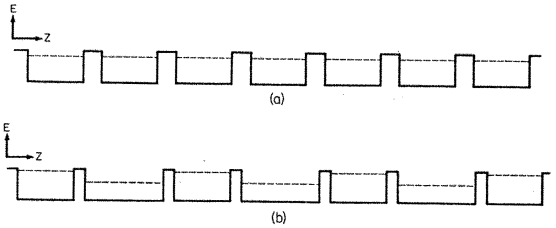

FIG. 1. Schematic illustration of the variation of the conduction-band edge with position in a periodic superlattice (a) and in a random super-structure of the "diatomic" type (b) considered here. The dashed lines are the energies W_n of bound states in the (isolated) quantum wells.

The dispersion relation in this model is

$$E(k_x,k_y,E_{z,i})=\hbar^2(k_x^2+k_y^2)/2m+E_{z,i} \ , \tag{3}$$

where $E_{z,i}$ is the ith eigenvalue of H_z.

With a random superstructure the matrix elements W_n and V_n become random variables, with distributions determined by the growth conditions. The Appendix shows how these tight-binding matrix elements are related to the well depths (i.e., alloy compositions) and thicknesses.

Writing the density of states

$$D(E)=N^{-1}\sum_{k_x,k_y}\sum_{E_{z,i}}\delta\left[E-\frac{\hbar^2(k_x^2+k_y^2)}{2m}-E_{z,i}\right] \tag{4}$$

and assuming effective-mass theory with a constant effective mass m throughout the superstructure,[15] we find that the derivative of the superstructure density of states is proportional to a one-dimensional density of states $\rho(E)$:

$$\frac{dD}{dE}=C\sum_{\epsilon_z}\delta(E-\epsilon_z)=CN^{1/3}\rho(E) \ , \tag{5}$$

where $C=(L/2\pi)^2\,(2m/\hbar^2)$ and the sample size is L^3. An alternative method for determining the one dimensional density of states $\rho(E)$ is to apply a strong magnetic field perpendicular to the superlattice layers and to condense the transverse free-electron motion into discrete Landau levels.

For the special case of a periodic superstructure, the eigenvalues are

$$E_z(k_z)=2V\cos ka_L \ , \tag{6}$$

where a_l is the distance between the centers of adjacent wells and E_n is taken to be zero for all n.

The densities of states are

$$\rho(E)=\pi^{-1}(4V^2-E^2)^{-1/2}\Theta(4V^2-E^2) \ , \tag{7a}$$

and

$$D(E)=\frac{1}{\pi}\left[\sin^{-1}\left[\frac{E}{2V}\right]+\frac{\pi}{2}\right]\Theta(4V^2-E^2) + \Theta(E-2v) \ , \tag{7b}$$

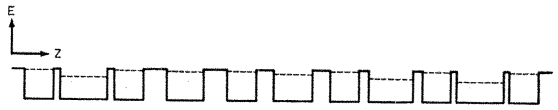

FIG. 2. Schematic illustration of the tight-binding model obtained for a random superstructure such as that in Fig. 1. (See Appendix.)

where $\Theta(x)$ is the unit step function. (See Fig. 3 for $A=0=B$.) Near the top and the bottom of the band for $\rho(E)$, the spectrum exhibits van Hove singularities[16] which behave like $|E-E_T|^{-1/2}$, where E_T is a threshold energy (± 2 V here); this is a characteristic of a one-dimensional density of states, which $\rho(E)$ is.

III. METHOD FOR EVALUATING $\rho(E)$

The tight-binding model Hamiltonian H_z for the random superstructure is a tridiagonal matrix

$$H_z=\begin{bmatrix} W_1 & V_1 & 0 & 0 & 0 & 0 & \cdots & & \\ V_1 & W_2 & V_2 & 0 & 0 & 0 & & & \\ 0 & V_2 & W_3 & V_3 & 0 & 0 & & & \\ 0 & 0 & V_3 & W_4 & V_4 & 0 & & & V_{N-1} \\ 0 & 0 & \cdots & & & & & V_{N-1} & W_N \end{bmatrix}, \tag{8}$$

and its secular determinant can be expressed in terms of its eigenvalues

$$\det(H_z-E)=\prod_i (E_{z,i}-E)\ . \tag{9}$$

This determinant can be evaluated by elementary row operations, and is

$$\det(H_z-E)=\prod_{n=1}^{N} X_n\ , \tag{10}$$

where $X_n=W_n-E-V_{n-1}^2/X_{n-1}$ is determined recursively, with X_1 being W_1-E.

The number of negative factors in Eq. (9) or (10) is the number of eigenvalues $E_{z,i}$ less than E, or the integrated density of states

$$S(E)=\int_{-\infty}^{E}\rho(E')dE'=ND(E)\ . \tag{11}$$

Thus the densities of states $D(E)$ and $\rho(E)$ can be determined by fixing E, counting the number of sign changes in Eq. (10), and differentiating. This is basically the negative eigenvalue theorem,[17] and can be used for *any* Hamiltonian of the form of Eq. (8). The numerical evaluation of the densities of states for very large superstructures is easy and computationally very fast.

IV. RESULTS

To illustrate this approach, we consider a simple example with a special kind of randomness: The nearest-neighbor matrix elements V_n are all equal, the odd-site diagonal matrix elements all vanish ($W_{2n-1}=0$), and the even-site matrix elements are uniformly but randomly distributed in the interval $[-A,B]$. Thus the disorder band width is $A+B$.

In this case we are especially interested in whether the disordered system exhibits a band gap. We know that for $A=-B$ the model does produce a gap (because we have a "diatomic crystal") and that for $A=B$ it does not (because $A=B$ would correspond to the Anderson model[3] if both even and odd sites were disordered). We hope to stimulate experiments studying the transition from Anderson to diatomic behavior.

The results for $\rho(E)$ are shown in Figs. 3–6. The calculations employed a model with 20 000 layers. We took $V=1$, and random disorder uniformly distributed within the interval $[-A,B]$. That is, the minimum energy of a disordered site is $-A$, and the maximum is B.

Several features of the calculated densities of states merit special mention: (i) For $A=B$ (the quasi-Anderson model) no gap appears (Fig. 3) the disorder simply makes the density of states curve flatter, broader, and more ragged as B increases. (ii) For $A=0$, the disorder is completely asymmetrical, the spectrum is shifted to higher energy, band tailing is evident near the bottom of the band, and a gap opens in the density of states for any finite B (Fig. 4). For small B, the density of states sprouts two van Hove singularities[16] on either side of the gap. As the disorder (B) increases, the van Hove singularities at the top and bottom of the perfect crystal density of states are attenuated, but the van Hove singularity at $E=0$ becomes sharper while the singularity at the gap first sharpens, then is blurred (Fig. 4). The gap occurs because the average or virtual crystal is diatomic. (iii) If the disorder width $A+B$ is kept constant, the gap narrows and the $E=0$ singularity disappears as the distribution of disordered levels becomes more

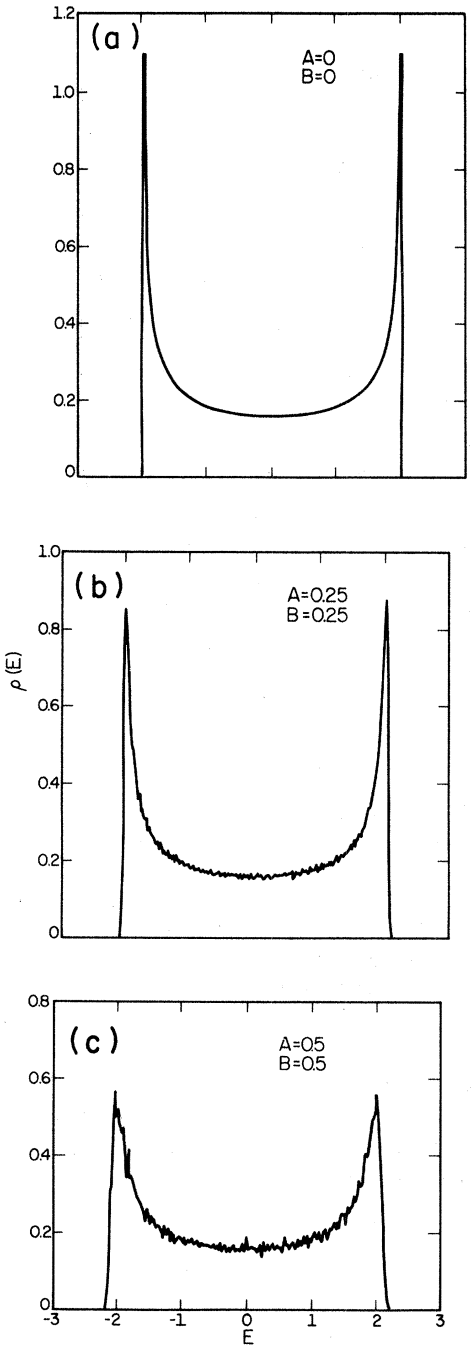

FIG. 3. Calculated densities of states $\rho(E)$ vs E for $A=B$, $V=1$.

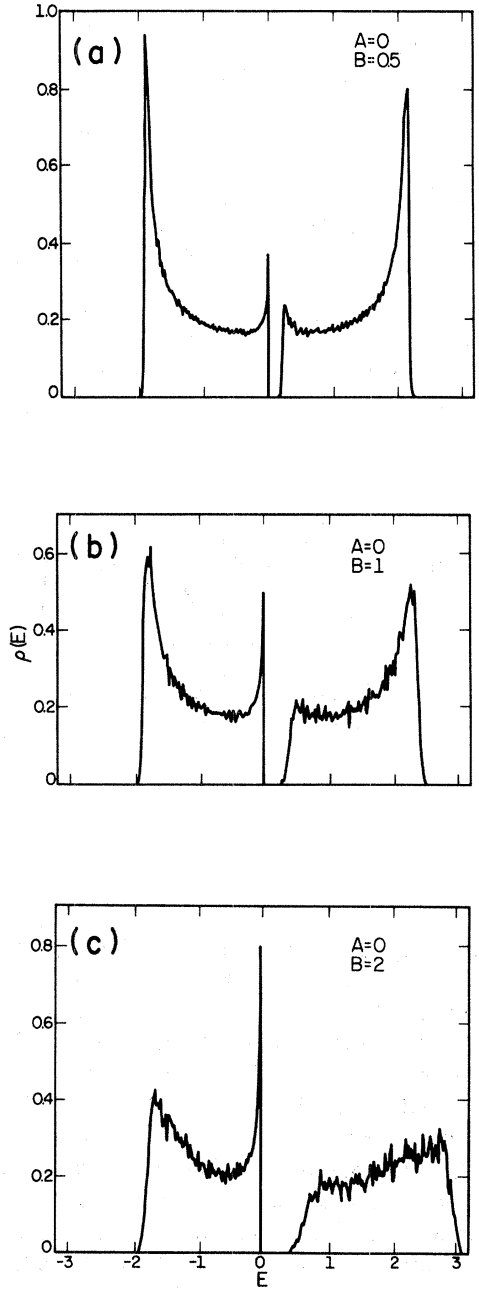

FIG. 4. Densities of states $\rho(E)$ vs E for $A=0$, $V=1$, and various values of B.

symmetrically distributed about $E=0$, the energy of the undisordered sublattice (see Fig. 5). Of course, the results are symmetric in A and B, as can be seen by comparing Fig. 6 and the corresponding curve of Fig. 4.

The gap is the most outstanding feature of this particular type of controlled randomness. In the Appendix we suggest some growth parameters for a superstructure likely to exhibit such a gap.

However, the primary purpose of this paper is to encourage and stimulate efforts to grow superlattices with controlled randomness or controlled imperfections. The cases we have considered here are but a few of the many conceivable.

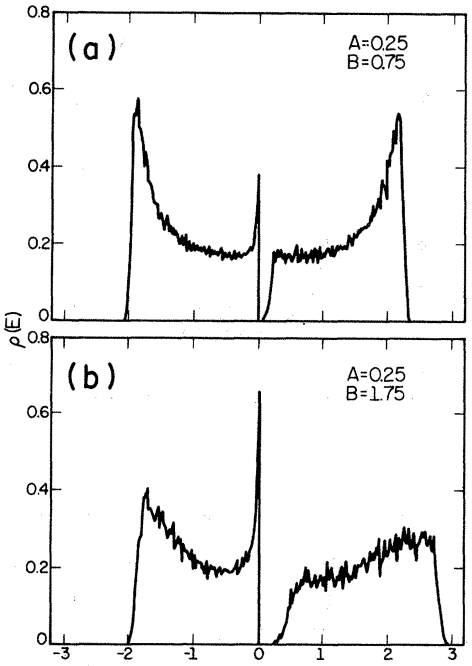

FIG. 5. Densities of states $\rho(E)$ vs E for band widths $A+B=1$ and 2, and with $V=1$.

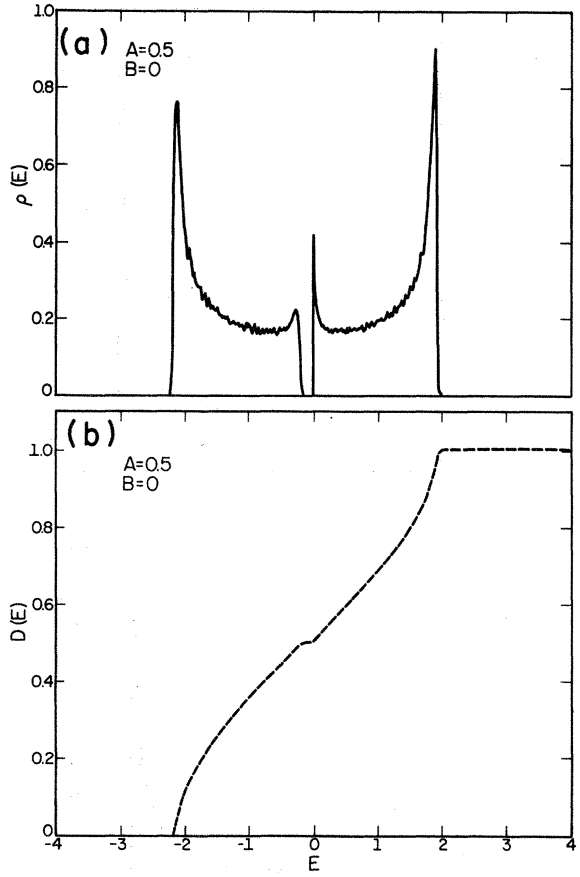

FIG. 6. Density of states $\rho(E)$ and full density of states $D(E)$ for $A=0.5$, $B=0$, and $V=1$. Compare this with Fig. 4 for $A=0$, $B=0.5$. The gap in $\rho(E)$ shows up as a flat portion in $D(E)$.

ACKNOWLEDGMENTS

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APPENDIX: DETERMINATION OF THE PARAMETERS OF THE TIGHT-BINDING MODEL

In this appendix we show how the matrix elements of the tight-binding model are related to the thicknesses and well depths of the quantum wells. A two-well element of the superlattice is shown in Fig. 7. The left well (e.g., GaAs) extends from z_n to Z_n, and has a depth $U_n=-|U_n|$ relative to the reference or "spacer" material (e.g., AlAs); the right well (e.g., $Al_{1-x}Ga_xAs$) extends from z_{n+1} to Z_{n+1}, with depth U_{n+1}. The Hamiltonian for the two-well system is[14] expressible in terms of the unit step function $\Theta(z)$:

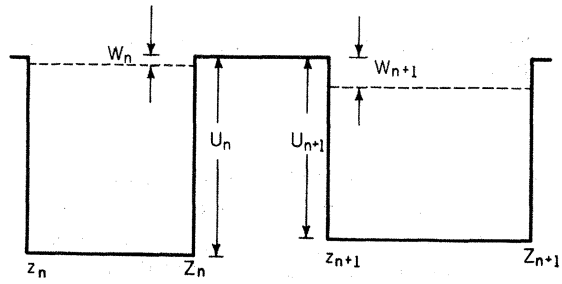

FIG. 7. Schematic illustration of the notation for the two-well model.

TABLE I. Parameters for the growth of a random superstructure of 400 layers. See Fig. 7 for the notation. The wells are made of GaAs and the barriers of $Ga_{0.5}Al_{0.5}As$. Z_{2n-1} is always 30.94 Å (for GaAs), and $z_{2n+1}-Z_{2n}$ is equal to $z_{2n}-Z_{2n-1}$.

Random number	$Z_{2n}-z_{2n}$ (Å)	$z_{2n}-Z_{2n-1}$ (Å)	Random number	$Z_{2n}-z_{2n}$ (Å)	$z_{2n}-Z_{2n-1}$ (Å)
0.195	50.51	7.55	0.145	51.65	6.70
0.732	39.24	24.91	0.235	49.60	8.28
0.609	41.78	18.30	0.999	31.31	581.16
0.323	47.68	10.01	0.100	52.72	5.98
0.108	52.52	6.11	0.374	46.59	11.14
0.188	50.65	7.44	0.831	37.11	34.29
0.062	53.66	5.38	0.413	45.76	12.09
0.713	39.64	23.63	0.233	49.64	8.24
0.638	41.18	19.58	0.589	42.18	17.49
0.049	53.98	5.18	0.828	37.16	33.97
0.671	40.52	21.19	0.013	54.87	4.65
0.392	46.20	11.57	0.557	42.82	16.32
0.379	46.48	11.26	0.170	51.09	7.12
0.538	43.20	15.68	0.131	51.98	6.48
0.884	35.84	43.56	0.033	54.37	4.95
0.409	45.84	11.99	0.571	42.54	16.83
0.800	37.80	30.65	0.566	42.64	16.65
0.436	45.29	12.66	0.044	54.11	5.10
0.020	54.71	4.75	0.226	49.81	8.11
0.134	51.92	6.52	0.735	39.19	25.08
0.679	40.35	21.63	0.557	42.82	16.33
0.391	46.22	11.55	0.660	40.74	20.64
0.298	48.21	9.50	0.522	43.52	15.16
0.182	50.80	7.33	0.236	49.57	8.30
0.366	46.76	10.95	0.663	40.67	20.81
0.136	51.88	6.55	0.849	36.67	37.02
0.686	40.20	22.04	0.294	48.29	9.43
0.306	48.04	9.66	0.006	55.05	4.55
0.457	44.86	13.22	0.802	37.75	30.88
0.369	46.69	11.03	0.430	45.42	12.51
0.956	33.75	76.21	0.185	50.73	7.38
0.117	52.32	6.24	0.523	43.51	15.19
0.432	45.38	12.56	0.932	34.52	59.86
0.267	48.88	8.89	0.056	53.80	5.29
0.037	54.27	5.01	0.884	35.82	43.69
0.470	44.59	13.58	0.511	43.75	14.81
0.362	46.85	10.86	0.427	45.48	12.43
0.439	45.24	12.74	0.923	34.78	55.66
0.555	42.87	16.24	0.664	40.66	20.83
0.747	38.94	25.96	0.453	44.95	13.11
0.038	54.25	5.02	0.057	53.79	5.30
0.109	52.51	6.12	0.985	32.52	135.17
0.574	42.47	16.95	0.278	48.64	9.11
0.873	36.10	41.26	0.715	39.60	23.77
0.883	35.86	43.30	0.148	51.59	6.75
0.405	45.94	11.87	0.956	33.74	76.47
0.665	40.63	20.89	0.862	36.38	39.10
0.305	48.06	9.64	0.999	31.41	453.33
0.288	48.42	9.31	0.966	33.37	88.00
0.352	47.05	10.65	0.901	35.40	47.86

$$\frac{-\hbar^2}{2m}\frac{d^2}{dz^2}+U_n\Theta(Z_n-z)\Theta(z-z_n)+U_{n+1}\Theta(Z_{n+1}-z)\Theta(z-z_{n+1}) .$$

The eigenvalue W_n is obtained, as for a single square well, from the transcendental equation:

$$(W_n-U_n)^{1/2}=(-U_n)^{1/2}\sin\left[\left[\frac{2m}{\hbar^2}(W_n-U_n)\right]^{1/2}\frac{(Z_n-z_n)}{2}\right] .$$

The tunneling operator V is evaluated in the WKB approximation, as by Harrison[12]:

$$|V_{n,n+1}|^2=\frac{\hbar^2}{4}v_nv_{n+1}/[(Z_{n+1}-z_{n+1})(Z_n-z_n)]\exp(-r_n) ,$$

where v_n is the electron's velocity in the nth well and we have

$$r_n=2(2m/\hbar^2)^{1/2}\int_{Z_n}^{z_{n+1}}(-W_n)^{1/2}dz .$$

For our case, this becomes

$$V_{n,n+1}=(\hbar^2/2m)^{1/2}(W_n-U_n)^{1/4}(W_{n+1}-U_{n+1})^{1/4}(Z_n-z_n)^{-1/2}(Z_{n+1}-z_{n+1})^{-1/2}\exp(-R_n) ,$$

where

$$R_n=(2m/\hbar^2)^{1/2}\int_{Z_n}^{z_{n+1}}\tfrac{1}{2}[(-W_n)^{1/2}+(-W_{n+1})^{1/2}]dz .$$

Thus the effective Hamiltonian of the two-well system becomes

$$H=|n\rangle W_n\langle n|+|n+1\rangle W_{n+1}\langle n+1|+|n\rangle V_{n,n+1}\langle n+1|+|n+1\rangle V_{n,n+1}\langle n| .$$

The relationships among the parameters W_n, $V_{n,n+1}$, U_n, Z_n, and z_n permit one to construct superstructures of the form discussed in this paper. For example, to grow a 400-layer random superstructure from alternating layers of GaAs and $Al_{0.5}Ga_{0.5}As$, with $B=2$, $A=0$, $V=1$, and a gap of ~ 0.04 eV, one might consider the thicknesses in Table I.

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[1]A. F. Blakeslee, J. Electrochem. Soc. 118, 1459 (1971); A. Y. Cho. Appl. Phys. Lett. 19, 467 (1971); L. Esaki and L. L. Chang, Phys. Rev. Lett. 33, 495 (1974).

[2]L. Esaki and R. Tsu, IBM J. Res. Dev. 14, 61 (1970).

[3]P. W. Anderson Phys. Rev. 109, 1492 (1958).

[4]H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. 44, 810 (1980).

[5]W. Kohn, *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 257.

[6]E. E. Mendez, L. L. Chang, G. Landgren, R. Ludeke, L. Esaki, and F. H. Pollak, Phys. Rev. Lett. 46, 1230 (1981).

[7]Localized states such as deep impurity levels do not obey an effective mass equation, and when localized near one of the many interfaces of a superstructure can differ significantly from the corresponding bulk states.

[8]A mixed localized-extended theory is appropriate for problems such as field ionization of deep impurity levels, where the initial state is localized but the final state is best described by effective mass theory.

[9]J. D. Dow *et al.* (unpublished).

[10]We assume that the quantum well is sufficiently narrow and shallow that it has exactly one bound state, i.e., $(h^2\pi^2/2m)<U_nL_n^2<(4h^2\pi^2/2m)$.

[11]J. Bardeen, Phys. Rev. 6, 57 (1961).

[12]W. A. Harrison, Phys. Rev. 123, 851 (1961).

[13]M. H. Cohen, L. M. Falicov, and J. C. Phillips, Phys. Rev. Lett. 8, 316 (1962).

[14]R. E. Prange, Phys. Rev. 131, 1083 (1963).

[15]For simplicity, we neglect the discontinuity of the effective mass across the interfaces of the superlattice.

[16]L. van Hove, Phys. Rev. 89, 1189 (1953).

[17]P. Dean, Proc. Phys. Soc. London 73, 413, (1959); Proc. R. Soc. London Sec. A 254, 507 (1960); 260, 263 (1961); D. N. Payton III and W. M. Visscher, Phys. Rev. 154, 802 (1967); H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, Cambridge, 1950), p. 140.