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DEVELOPMENTS OF THE LOCAL APPROXIMATION FOR DISORDERED SYSTEMS

W. KOHN and J. OLSON

Dept. of Physics, University of California, San Diego, La Jolla, California 92037, U. S. A.

Abstract. — The local approximation (LA) for the electronic structure of disordered systems, proposed by Butler and Kohn, is further developed. Analysis of the moments of the density of states and numerical application to the model of Velicky et al. allow comparison with the coherent potential approximation (CPA). The results of the two approximations differ substantially, the LA showing considerable structure where the CPA shows none. A preliminary discussion of this discrepancy is presented. The possibilities of using the LA for quantitative calculations of realistic alloy models are briefly discussed.

1. Introduction. — This paper represents a contribution to the theory of single electron states in strongly disordered alloys. In particular we shall be interested in a model in which there are regularly situated atomic sites, but in which these sites are occupied in a random manner by two kinds of atoms, A and B, with potentials \( v_A \) and \( v_B \).

As the Schroedinger equation for such a system cannot be exactly solved one is forced to adopt some approximation method. A natural point of view is to regard the actual system as equivalent in lowest approximation to a periodic system in which both \( v_A \) and \( v_B \) are replaced by a well-chosen common potential \( v_0 \). This point of view underlies several useful schemes: The rigid band model [1], perturbation expansion of the self energy [2], the averaged \( t \)-matrix approximation [3], [4], and the coherent potential approximation (CPA) [5]-[9].

Particularly the CPA, in which the effective common potential \( v_0 \) is chosen self-consistently, has been shown to give useful results over a wide range of parameters (see especially VKE, [9]) and has proved to be very fruitful in recent years. Nevertheless we wish to draw attention to the fact that methodologically the small parameters occurring in the CPA and the other approximations mentioned above, are the difference between the atomic potentials \( v_A \) and \( v_B \) (or of the corresponding \( t \)-matrices) and the concentration of one of the constituents (1). They therefore do not constitute the "natural" approximation for the case of a strongly disordered alloy in which atoms A and B differ strongly in their scattering characteristics and have comparable concentrations.

An approximation scheme which works best in the limit of the strongly disordered alloy has recently been proposed [10]. We shall use the term "local approximation" (LA) for this scheme. It is based on the quite primitive idea that in a disordered system the physical conditions at a point \( r \) depend significantly only on the conditions inside a rather small neighborhood, \( |r' - r| < R \), where \( R \) is of the order of the smaller of the following two quantities: a characteristic De Broglie wavelength \( \lambda \) and a mean free path \( l \). The effects of the more distant environment fall off exponentially with distance. Thus, particularly for a strongly disordered infinite alloy, physical properties should be calculable by suitably averaging over quite small local neighborhoods. These qualitative ideas have been to some extent developed theoretically in BK [10], where also numerical applications to one dimensional systems were reported.

In the present paper we begin, in Sec. 2, with a description of the model which will be used and explain how one applies the LA to it. An analysis of the moments of the density of states for the model is given in Sec. 3, including a comparison with the CPA. Sec. 4 gives the numerical results of applying the LA and CPA to a simple cubic tight binding alloy. Sec. 5 contains concluding remarks, including a discussion of possible future applications of the LA. An appendix deals with statistical aspects of the LA.

2. The model and the method. — In order to obtain some perspective of the capabilities and limi-
tations of the LA approach and to facilitate comparison with the CPA we adopt here the model of VKE to which we refer for details. We do this in spite of the fact that it is not fully characteristic of the general three-dimensional problem. The Hamiltonian of this model is

\[ \mathcal{H} = \sum_n |n > e_n < n| + \sum_{n \neq m} |m > t_{nm} < n| \equiv D + W. \]  

\[ (2.1) \]

Here \(|n >\) denotes an atomic orbital associated with the site \(n\); \(e_n\) its energy when isolated; \(t_{nm}\) is a coupling term independent of composition; and \(D\) and \(W\) denote the site-diagonal and site-off-diagonal of \(\mathcal{H}\). \(e_n\) assumes one of the two values

\[ e_A = e_0, \quad e_B = - e_0 \]  

\[ (2.2) \]

for A and B atoms respectively. We further consider only nearest neighbor coupling (an approximation not made in VKE) and write

\[ t_{nm} = \begin{cases} t & \text{for nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \]  

\[ (2.3) \]

The operator \(W\) is diagonal in the \(k\)-representation, and can be written as

\[ <k | W | k'> = \delta_{kk'} \omega_S(k); \]  

\[ (2.4) \]

here

\[ |k > = N_0^{-1/2} \sum_n e^{ikn} |n > \]  

\[ (2.5) \]

where \(N_0\) is the total number of atoms, and

\[ \omega_S(k) = t \sum_{\text{nearest neighbors}} e^{ikn}. \]

\[ (2.6) \]

The constant \(w\) is chosen so that

\[ \max s(k) - \min s(k) = 2. \]

\[ (2.7) \]

For example, in a simple cubic lattice

\[ w = 6t, \]

\[ s(k) = \frac{1}{2} (\cos k_x a + \cos k_y a + \cos k_z a). \]

\[ (2.8) \]

The function \(\omega_S(k)\) describes the pure A or B band relative to \(e_A\) and \(e_B\). We shall take its half-width, \(w\), as unit of energy; thus

\[ w = 1. \]

\[ (2.9) \]

The principle of the calculation is now extremely simple (see BK). For any given lattice fill the entire space with identical \(v\) super-cells \(c\), each containing say \(N\) lattice sites (Fig. 1). Now consider (temporarily) the super-cell at the origin as closed on itself. There exist \(2^v\) ways of populating the \(v\) sites with A and B atoms. Give each configuration \(c\) with \(v_1\) A-atoms and \(v_2 = v - v_1\) B-atoms the weight

\[ w_c = x^{v_1} y^{v_2}. \]

\[ (2.10) \]

for all configurations \(c\).

Having populated the central cell in a certain configuration, populate all other cells identically (i.e. by translation of the configuration \(c\)). The result is a periodic crystal structure \(S(v, c)\) whose unit cell contains \(v\) atoms. Now calculate by standard methods the normalized density of states \(\rho_c(E)\) of this periodic structure and then average over \(c\)

\[ \rho^{(v)}(E) \equiv <\rho_c(E)>_c. \]

\[ (2.11) \]

Finally, the density of states, \(\rho(E)\), of the infinite alloy, which we denote simply by \(S\), is given by

\[ \rho(E) = \lim_{v \to \infty} \rho^{(v)}(E). \]

\[ (2.12) \]

Since this convergence has been shown in BK to be exponential we shall in practice take

\[ \rho(E) \approx \rho^{(v_0)}(E) \]

\[ (2.13) \]

where \(v_0\) is sufficiently large.

3. Moments. — Some insight into the convergence of the LA can be obtained from a study of the moments

\[ \mu_p = \int dE E^p \rho(E) = \frac{1}{N_0} \text{Tr} < H^p >_s \]

\[ = \frac{1}{N_0} \text{Tr} < (D + W)^p >_s \]  

\[ (3.1) \]
where $< >_{av}$ denotes average over the configurations $c$. Because of the equivalence of all sites, (3.1) can also be written as

$$
\mu_p = < < 0 | (D + W)^p | 0 > >_{av}. \tag{3.2}
$$

Now consider a typical term in the binomial expansion of (3.2), such as the term

$$
X = < 0 | D W D W | 0 >_{av}, \tag{3.3}
$$

occurring in $\mu_s$. This may be developed in the form

$$
X = \sum \left(< < 0 | D | 0 > < 0 | W | n_1 > < n_1 | D | n_1 > < n_1 | W | n_2 > < n_2 | W | 0 > > >_{av}, \right) \tag{3.4}
$$

and each term in the last sum can be associated with the 5 step path $0 - 0 - n_1 - n_1 - n_2 - 0$. $D$ puts a point into the same place and $W$ moves it to a nearest neighbor. Since

$$
< < n | D | n > 2m + 1 >_{av} = 0 \tag{3.5}
$$

only those terms involving $< n | D | n > 2m$ contribute to $\mu_p$.

Now compare the moments $\tilde{\mu}_p$ of the crystal structure $S(v, c)$ consisting of the periodically repeated super-cell of the LA, with the moments $\mu_p$ of the actual infinite alloy, $S$. The eq. (3.1) also determines $\tilde{\mu}_p$, but the average must now be evaluated over the configurations of the periodically repeated crystal structure $S(v, c)$. This contains the incorrect correlations,

$$
< < n + \tau | D | n + \tau > = < < n | D | n > \tag{3.6}
$$

where $\tau$ is a translation vector of the structure $S(v, c)$. We now ask which is the lowest moment for which the correlation (3.6) introduces an error. Because of the trace in (3.1) we can restrict ourselves to terms, like $X$, eq. (3.3), in which the first factor is $D$ (2). Then if $s$ nearest neighbor steps are required to pass from 0 to $\tau$, the first incorrect contributions come from

$$
< 0 | D | 0 > < 0 | W^s | \tau > < \tau | D | \tau > < \tau | W^s | 0 > \tag{3.7}
$$

which occurs in the moment, $p = 2s + 2$. Thus we see that

$$
\tilde{\mu}_p = \mu_p \quad p = p_0 \quad \frac{p_0}{2} \quad 1. \tag{3.8}
$$

For example consider a simple cubic alloy. Table I lists the number of lattice points $v$ in super-cells of various shapes and the corresponding number of exact moments. Tables II and III give the same information for body-centered cubic and face centered cubic alloys.

These results may be compared to the CPA for which the number of exact moments is 7 (3). In order to exceed this number by the LA, super-cells with $v \geq 16$ are required. Such cells are large enough to contain in their interior the central atom and all its nearest neighbors.

We wish to emphasize that these results are true regardless of the degree of disorder. For a highly disordered lattice, however, we expect that an LA calculation, even with small $v$, will give rather accurate-though not exact results for $\mu_p$ with $p > p_0$. In addition, no matter how small $v$ is, the method evidently gives exact results in the weak disorder limit, up to first order in $E_0 = \frac{1}{2} (E_A - E_B)$.

To illustrate these facts we calculate for $v = 1, 2, 4$, SC lattice, the first inexact moment, $\tilde{\mu}_p$, of the local approximation and the corresponding exact moment, $\mu_p$ (cf. Table I).

$$
\begin{align*}
&v = 1 \quad \mu_4 = \frac{3}{2} + 24 \frac{e_0}{2} t^2 + 90 t^4 \\
&\tilde{\mu}_4 = \mu_4 + 24 \frac{e_0}{2} t^2 \\
&\left( \frac{\tilde{\mu}_4}{\mu_4} \right)^{1/4} = 1.12 \quad \text{at} \quad e_0 = 3.08 \quad t = 1.02 \quad w
\end{align*}
$$

Table I

<table>
<thead>
<tr>
<th>No of Atoms, $v$, per super-cell</th>
<th>Shape of super-cell</th>
<th>No of exact moments, $p_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 SC</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>FCC</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>BCC</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>SC</td>
<td>5</td>
</tr>
<tr>
<td>16</td>
<td>FCC</td>
<td>9</td>
</tr>
</tbody>
</table>

Table II

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<tr>
<th>No of Atoms, $v$, per super-cell</th>
<th>Shape of super-cell</th>
<th>No of exact moments, $p_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BCC</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>SC</td>
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<td>5</td>
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<td>SC</td>
<td>9</td>
</tr>
</tbody>
</table>

Table III

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<tr>
<th>No of Atoms, $v$, per super-cell</th>
<th>Shape of super-cell</th>
<th>No of exact moments, $p_0$</th>
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<td>16</td>
<td>BCC</td>
<td>9</td>
</tr>
</tbody>
</table>

(2) Terms in which $D$ does not occur cannot introduce an error.

(3) VKE and private communication from F. Brouers.
We note that the maximum errors of the first inexact moments are relatively small. We also note that these errors are positive. This is due to the fact that configurations of low probability corresponding to the tails of $p(E)$, are over-emphasized in the LA.

One final remark concerns the great value of continuing the super-cell periodically. Suppose, instead, we had simply closed one super-cell on itself and determined the corresponding eigenvalues. We can easily analyze the moments for this case also. One finds directly that if $s$ is the number of steps required to go from one site, once $N_\infty>\infty$ the self-closed cell back to the same site $s$, the first incorrect moment $\tilde{\mu}_1$ now corresponds to $p = s + 2$, rather than $2s + 2$ for the periodically continued super-cell. The periodically continued lattice will thus give moments which are vastly better, without making the calculations significantly more difficult.

4. Numerical applications to the simple cubic lattice. — The theory outlined in Sec. 2 was applied to a simple cubic alloy of cube edge $a$, with equal concentrations of A and B atoms, and nearest neighbor interactions. For $\varepsilon_A = \varepsilon_B = 0$, the case of a periodic cubic lattice, the energy eigenvalues are

$$E_\varepsilon(k) = \frac{1}{2}(\cos k_x a + \cos k_y a + \cos k_z a)$$

(cf. eq. (2.3)-(2.9)). We have performed calculations for several values of the perturbation parameter

$$\varepsilon_0 \equiv \varepsilon_A = -\varepsilon_B.$$  \hspace{1cm} (4.2)

1. $\varepsilon_0 = 0$, the periodic case. 2. $\varepsilon_0 = \frac{1}{2}$, a fairly weakly perturbed lattice. 3. $\varepsilon_0 = 1$, a strongly perturbed lattice, with the eigenvalues just split into two sub-bands, one around $\varepsilon_A$, the other around $\varepsilon_B$. 4. $\varepsilon_0 = 2$, a very strongly perturbed lattice, with states in the upper and lower sub-bands being localized mostly near A- and B-atoms, respectively. Calculations were performed with super-cells containing $\nu = 1, 2, 4, 8, 16$ atoms. In each case $N = 10,000$ eigenvalues were computed. Because of the symmetry of the band, we can associate with each eigenvalue $E$ its negative, $-E$, which results in a total of 10,000 eigenvalues for each half band. The corresponding densities of states $\rho^{(0)}(E)$ were obtained by the smoothing procedure described in the appendix. For the case $\varepsilon_0 = 1$ they are exhibited in figures 2-6. Since all $\rho^{(0)}(E)$ are even functions of $E$, these functions are shown only for $E \geq 0$.

For $\nu = 1$,

$$\rho^{(1)}(E) = \frac{1}{2} \left[ \rho_0(E - \varepsilon_A) + \rho_0(E - \varepsilon_B) \right], \hspace{1cm} (4.3)$$

where $\rho_0$ is the unperturbed ($\varepsilon_0 = 0$) density of states, and figure 2 shows the approximate density of states obtained with 10,000 eigenvalues and smoothing, along with exact values taken from calculations of the periodic cubic lattice [11]. For this case we find

$$\frac{\rho^{(1)}(E)}{\rho_{\text{mea}}} = 0.064 \pm 2. \hspace{1cm} (4.4)$$

This is in general agreement with the estimates of the Appendix. For larger $\nu$, where the density of states exhibits more structure, the error will be somewhat larger.

In figure 3 a singularity will be seen at $E = \varepsilon_A = 1$. This comes from the configuration A-B describing an fcc NaCl structure. In the tight-binding approximation for such a structure there are band edges at $\pm \varepsilon_0$ at which there are accidentally strong $(E \mp \varepsilon_0)^{-1/2}$ Van Hove singularities. In general the density of

FIG. 2. — The curve represents the density of states for $\nu = 1$, obtained with 10,000 eigenvalues, the points are from an exact calculation [11]. $\sqrt{5} \sigma = 0.046$.

FIG. 3. — The density of states for $\nu = 2$, obtained with 10,000 eigenvalues. $\sqrt{5} \sigma = 0.021$. 

(4) This is equivalent to continuing the cell periodically but retaining only the eigenvalues corresponding to $k = 0$.

(5) For a given super-cell, this is the same $s$ which was introduced earlier in this section.
states, though non-analytic, remains finite at these singular points. Thus the appearance of the spurious infinity should not cause undue alarm concerning the LA in general.

In figure 4, we show in addition to the smoothed \( \rho^{(4)}(E) \), obtained with 10,000 eigenvalues, also the smoothed density obtained with a second set of 10,000 eigenvalues. The discrepancies between these densities, whose mean value is

\[
\frac{\langle \delta \rho^2 \rangle^{1/2}}{\rho_{\text{mean}}} = 0.0882 \tag{4.5}
\]

give a direct measure of the error due to fluctuations.

Figure 6 shows the results for our largest super-cell, \( v = 16 \). For such a large cell each atom and all its 6 nearest neighbors are statistically independent; in addition there are 8 statistically independent atoms among the 20 atoms on the next two shells and 1 among the 6 following. Also the five even moments \( \mu_0, \mu_2, \ldots, \mu_8 \) are given exactly (for \( N \to \infty \)) and all odd moments vanish, as they should. Finally, for \( \varepsilon_0 = 1 \), we expect a very short mean free path, of the order of 1 or 2 cube edges. For all these reasons we expect \( \rho^{(16)}(E) \) to be a good representation of the true \( \rho(E) \). Fluctuation errors, which are not shown on this figure, are very similar to the case of \( v = 4 \), figure 4. We wish to emphasize that our smoothing procedure has a slight tendency to attenuate structure in \( \rho \), but can never introduce any. So where structure appears above the fluctuation «noise» it is a real property of the super-cell «alloy» in question. In this sense three strong peaks are clearly present. Presumably these peaks correspond to certain types of configuration but at this time we have not yet adequately analyzed this correspondence. The curve shows a tendency to symmetry about \( E_A = 1 \); a symmetry about \( E_A \) is in fact present for \( (E_A - \varepsilon_0) \to \infty \) and increased symmetry has indeed been observed in our calculations for \( E_A = 2 \). We observe also that although eigenvalues can occur over the energy range \( 0 < E < 2 \), the density of states is in fact concentrated over a rather narrower energy range since the configurations and k-vectors corresponding to the energy extremes are very rare.

On the same figure 6 we also show, for comparison, the result of a single-site CPA calculation \((6)\). The contrast is very striking since \( \rho_{\text{CPA}} \) is completely structureless.

Of course both \( \rho^{(16)}_{\text{LA}}(E) \) and \( \rho_{\text{CPA}}(E) \) are only approximations to the correct \( \rho(E) \) and since they are so different an important question is which is the more nearly correct one. We are not yet in a position to answer this question conclusively. However, we can present a preliminary discussion:

The following considerations support the LA:

1) \( \rho^{(16)}_{\text{LA}} \) has a larger number of exact moments than \( \rho_{\text{CPA}} \).

2) The main structure in \( \rho^{(16)}_{\text{LA}} \) cannot be spuriously due to statistical fluctuations, which are much smaller, or to our smoothing procedure, which can by its nature only reduce the degree of structure.

3) Preliminary calculations of \( \rho^{(132)}_{\text{LA}} \) indicate a three peak structure much like that of \( \rho^{(16)}_{\text{LA}} \), with the total intensity in the central peak being very similar.

\((6)\) This curve was computed by Mr. M. Rao; cf. ref. [5]-[9], especially [9].
Nevertheless, we cannot rule out that as $v \to \infty$ most of the structure of $\rho^{(v)}(E)$ may eventually disappear. Preliminary calculations in the split limit $(\varepsilon_A - \varepsilon_B) \to \infty$, A- and B-lattices uncoupled) indicate that the central peak of $\rho^{(16)}(E)$ near $\varepsilon_A$ becomes a $\delta$-function at $\varepsilon_A$. If one separates the cubic lattice into 2 interpenetrating face-centered lattices, most (if not all) eigenfunctions with $E = \varepsilon_A$ have a finite amplitude on only one sublattice. (These functions do not require configurations in which the A-atoms form isolated clusters.) The importance of such states should decrease as $v \to \infty$. However, it is clear that at least a finite, though small, fraction of the integrated intensity, corresponding to isolated clusters of A-atoms, must remain in the form of $\delta(E - \varepsilon_A)$, even as $v \to \infty$. Whether there will also be a considerable intensity for $E$ near, but not at, $\varepsilon_A$ is not yet known.

Finally we may remark that if the structure in $\rho^{(16)}(E)$ is real, it is almost certainly due to special configurations involving several atoms. The CPA, being a mean field theory, could not represent such configurations, just as it does not yield the small $\delta(E - \varepsilon_A)$ portion of $\rho(E)$, due to isolated clusters, which is known to be present.

5. Concluding remarks. — In this paper we have studied the local approximation for a simple alloy model. Using 16 atoms per unit cell we find that in the local approximation there are more exact moments than in the coherent potential approximation. The local approximation gives a density of states with a mean field theory, could not represent such configurations, just as it does not yield the small $\delta(E - \varepsilon_A)$ portion of $\rho(E)$, due to isolated clusters, which is known to be present. It is not yet clear whether this result is real or spurious.

The computing time for the results shown in the figures was approximately 1-1/2 hours on a CDC 3600. Over 1 hour of this time was used for the case $v = 16$ which required the solution of 625 $16 \times 16$ hermitian complex secular equations. We believe that when our programs are optimized this time could be cut by about a factor of 2.

We plan to extend somewhat further the analysis of the local approximation applied to the model of VKE [9]. If we remain satisfied with the potentialities of this method we plan to apply it to realistic alloys, using the KKR method [12], [13]. Inclusion of s-, p-and d-states within the muffin-tin and use of a supercell with $v = 16$ atoms will lead to secular equations of dimension $144 \times 144$. Thus by taking advantage of the capabilities offered by contemporary computers we may be able to make progress towards a quantitative theory of the electronic structure of alloys.

Appendix: The statistical problem. — Suppose we have chosen a certain super-cell, with $v$ atoms and wish to determine the corresponding density of states $\rho^{(v)}(E)$. This leads to a statistical problem which is the subject of this appendix.

First of all, in this section, since we shall be dealing with one super-cell at a time, we shall not explicitly indicate the superscript $v$. Denote the volume in k-space of the fundamental Brillouin zone corresponding to the super-cell by $\Omega$; denote the eigenvalues corresponding to configuration $c$ and wave vector $k$ by $E_c(k)$; and let $\Delta Q_c(E)$ be the volume in k-space in which

$$E - \frac{\Delta E}{2} < E_c(k) < E + \frac{\Delta E}{2}.$$  \hspace{1cm} (A.1)

Then

$$\rho(E) = \sum_{c} w_c \rho_c(E)$$  \hspace{1cm} (A.2)

where

$$\rho_c(E) = \lim_{\Delta E \to 0} \frac{\Delta Q_c(E)}{\Delta E}. \Omega.$$  \hspace{1cm} (A.3)

In our case $w_c$ has the trivial common value of $2^{-v}$. So the problem is to find $\rho_c(E)$ for all 2$^v$ configurations $c$.

In principle this could be done by a sufficiently fine quantization of k-space, giving $\mathcal{N}$k-values in $\Omega$, and evaluating all $E_c(k)$. Then

$$\rho_c(E) = \frac{\text{Number of eigenvalues in the interval (4.1)}}{v^N}, \hspace{1cm} (A.4)$$

where the denominator represents the total number of eigenvalues. In practice, however, $\mathcal{N}$ would have to be taken in the range of $10^3 - 10^6$, and, say for $v = 8$, the total number of configurations is 256 so that a total of $2 \times 10^5$ to $2 \times 10^8$ eigenvalues would need to be evaluated — a prohibitive task.

An effective way of dealing with this difficulty is the Monte Carlo method. We choose at random a configuration $c'$ and a vector $k'$ and evaluate and record the $v$ corresponding eigenvalues; then we repeat with a second randomly chosen $c''$ and $k''$, etc., until a total of say $N$ eigenvalues, $E_1, E_2, \ldots, E_N$ has been accumulated. This set of eigenvalues is now taken to define a discontinuous Monte Carlo density of states,

$$\rho_{MC}(E; N) = \frac{1}{N} \sum_{n=1}^{N} \delta(E - E_n). \hspace{1cm} (A.5)$$

The actual density of states is given by

$$\rho(E) = \lim_{\Delta E \to 0} \frac{1}{\Delta E} \lim_{N \to \infty} \int_{E-\Delta E/2}^{E+\Delta E/2} \rho_{MC}(E'; N) \, dE'. \hspace{1cm} (A.6)$$

In practice we must of course stop after a finite number, $N$, of eigenvalues, and the question is how to obtain from the corresponding $\rho_{MC}(E; N)$ a good approximation to $\rho(E)$.

Acknowledgment. — We would like to thank Mr. M. Rao for carrying out the CPA calculations for comparison with our LA results. This work was supported in part by the US Office of Naval Research and the National Science Foundation.
For this purpose we introduce for each energy $E$ a narrow smoothing function, $f(E' - E ; \sigma(E))$, of width $\sigma(E)$, of the form

$$f(E' - E ; \sigma(E)) \equiv \frac{1}{\sigma(E)} \varphi \left( \frac{E' - E}{\sigma(E)} \right). \quad (A.7)$$

with the properties

$$\int f(E' - E ; \sigma(E)) \, dE' = 1 \quad (A.8)$$
$$\int f(E' - E ; \sigma(E)) \, (E' - E) \, dE' = 0 \quad (A.9)$$
$$\int f(E' - E ; \sigma(E)) \, (E' - E)^2 \, dE' = \sigma(E)^2. \quad (A.10)$$

We note that

$$\lim_{\sigma \to 0} f(x, \sigma) = \delta(x). \quad (A.11)$$

With this $f$ we now define a smoothed density function.

$$\tilde{\rho}(E) = \int f(E' - E ; \sigma(E)) \rho_{MC}(E') \, dE' = \frac{1}{N} \sum_{n=1}^{N} f(E_n - E ; \sigma(E)), \quad (A.12)$$

and wish to determine $f$ such that, for a given $N$, $\tilde{\rho}(E)$ represents a good approximation to the actual $\rho(E)$. Now $\tilde{\rho}(E)$ has errors from two sources.

1) A smoothing error, $\delta \rho_{sm}(E)$, remaining even in the limit as $N \to \infty$, due to the finite width $\sigma$ of $f$.

2) A fluctuation error, $\delta \rho_{fl}$, due to the randomness of the eigenvalues $E_n$ entering (A.12).

These are easily calculated. To estimate $\delta \rho_{sm}$ we go to the limit $N \to \infty$ and obtain from (A.10)

$$\delta \rho_{sm}(E) =$$

$$= \int f(E - E' ; \sigma(E)) \rho(E') \, dE' - \rho(E)$$

$$= \int_{-\infty}^{\infty} f(E - E' ; \sigma(E)) \left[ \rho(E) + (E' - E) \, \rho'(E) + \frac{1}{2} (E' - E)^2 \, \rho''(E) \right] \, dE' - \rho(E)$$

$$= \frac{1}{2} \rho'(E) \, \sigma(E)^2. \quad (A.13)$$

Turning next to $\delta \rho_{fl}$ we note that the mean value of the sum in (A.12) over all sets $\{E_1, ..., E_N\}$ is

$$\langle \sum_{n=1}^{N} f(E - E_n) \rangle_{av} =$$

$$= N \int f(E - E') \, \rho(E') \, dE' \approx N \rho(E). \quad (A.14)$$

Because of the randomness of the eigenvalues this quantity will fluctuate about its mean. Thus

$$\langle \left( \sum_{n=1}^{N} f(E - E_n) \right)^2 \rangle_{av} =$$

$$= N^2 \rho(E)^2 + N \rho(E) \int f^2(E - E') \, dE'. \quad (A.15)$$

This last integral is inversely proportional to the width $\sigma$

$$f^2(E - E') \, dE' = \gamma \sigma(E)^{-1} \quad (A.16)$$

where $\gamma$ is a numerical constant depending on the functional form of $f$. Thus the error of $\rho(E)$ due to statistical fluctuations is given by

$$< \delta \rho_{fl}^2 >_{av} = \frac{\gamma}{[\sigma(E) N]} [\rho(E)]. \quad (A.17)$$

Combining (A.10) and (A.14) gives finally for the total root-mean square error

$$< \delta \rho^2 >_{av} = < \delta \rho_{sm}^2 + \delta \rho_{fl}^2 >_{av} = \frac{\rho''}{4} \sigma^2 + \frac{\gamma}{\sigma N} \rho. \quad (A.18)$$

It will be observed that the smoothing error increases with $\sigma$ while the fluctuation error decreases with $\sigma$. The total error is minimized by choosing

$$\sigma = \frac{\gamma^{1/5} \rho^{1/5}}{\rho''^{1/5} N^{1/5}} \quad (A.19)$$

and the corresponding root mean square error of $\rho$ is

$$< \delta \rho >_{r.m.s.} = \left( \frac{5}{4} \gamma^{2/5} \rho''^{2/5} \rho'^{1/5} \right) \frac{1}{N^{2/5}}. \quad (A.20)$$

The $N^{2/5}$, instead of the customary $N^{1/2}$, is due to the fact that if $N$ increases $\sigma$ decreases as $N^{-1/5}$, so that $\sigma^4$ and $\sigma N$ both behave as $N^{4/5}$.

Next we look for the functional form of $f$ which minimizes $\gamma$. This is the solution of the following variational problem:

$$\int f^2(x) \, dx = \text{minimum}, \quad (A.21)$$

subject to the conditions

$$\int f(x) \, dx = 1, \quad \int f(x) \, x^2 \, dx = \sigma^2. \quad (A.22)$$

Using the conventional method of Lagrange multipliers gives

$$f(x) = \begin{cases} \frac{3}{4 \times 5^{1/2} \sigma} \left[ 1 - \frac{x^2}{5 \sigma^2} \right] & |x| < \sqrt{5} \sigma \\ 0 & |x| > \sqrt{5} \sigma \end{cases} \quad (A.23)$$

and

$$\gamma = \frac{3}{5^{3/2}} = 0.2683. \quad (A.24)$$
Other, reasonable, choices of \( f(x) \) give quite similar values of \( y \). For example, a square wave gives
\[
y = 12^{-1/2} = 0.289.
\]

With the function \( f(x) \) given by (A.23) and \( y \) by (A.24), eq. (A.19) and (A.20) become
\[
\sigma = 0.769 \frac{\rho^{1/5}}{|\rho''|^{2/5}} \frac{1}{N^{1/5}}, \quad (A.25)
\]
\[
\langle \delta \rho \rangle_{r.m.s.} = 0.660 \rho^{2/5} |\rho''|^{1/5} \frac{1}{N^{2/5}}. \quad (A.26)
\]

For quantitative orientation consider the density function
\[
\rho(E) = \frac{3}{2D} \left( 1 - \frac{4E^2}{D^2} \right), \quad (A.27)
\]
which has a single maximum and extends over the interval \((-D/2, +D/2)\). At \( E = 0 \), where \( \rho \) has its maximum,
\[
\rho = \frac{3}{2D}, \quad |\rho''| = \frac{12}{D^3}. \quad (A.28)
\]
Therefore, by (A.16),
\[
\sigma = \frac{0.316}{N^{1/5}} D, \quad \langle \delta \rho \rangle_{r.m.s./\rho\text{mean}} = \frac{1.28}{N^{2/5}}. \quad (A.29)
\]
Table IV lists some representative values.

### Table IV

<table>
<thead>
<tr>
<th>( N )</th>
<th>( \sigma/D )</th>
<th>( \langle \delta \rho \rangle_{r.m.s./\rho\text{mean}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^3 )</td>
<td>0.079</td>
<td>8.1 \times 10^{-2}</td>
</tr>
<tr>
<td>( 10^4 )</td>
<td>0.050</td>
<td>3.2 \times 10^{-2}</td>
</tr>
<tr>
<td>( 10^5 )</td>
<td>0.032</td>
<td>1.3 \times 10^{-2}</td>
</tr>
</tbody>
</table>

In order to determine \( \sigma(E) \) from (A.19), one requires a rough knowledge of \( \rho(E) \) and \( \rho''(E) \), already before smoothing. This can be done by a rough preliminary histogram. Since the error \( \delta \rho \) has a minimum for \( \sigma \) given by (A.19), it will not be increased unduly if \( \sigma \) is slightly different. In practice we have taken \( \sigma \) about \( 2/3 \) of the value calculated according to (A.19) with rough estimates for \( \rho \) and \( \rho'' \). This increases the theoretical error by only 11 percent, and lessens the chance of obliterating real details of \( \rho(E) \).

**Addendum in proof.** — We can now give a quantitative account of the origin of the excessively large central peak in the density of states which is found even for quite large clusters. The excess fractional strength of this peak disappears as \( v^{-1/2} \) where \( v \) is the number of atoms in the cluster.

In the split band limit let us consider, for example, the A-band. Let \( M_I \) be the number of A-atoms on sublattice I (see end of Sec. 4), and \( M_{II} \) the number on sublattice II. Suppose \( M_I \approx M_{II} \). We reckon energies from \( \epsilon_d \). For a solution with wave-vector \( k \), the tight-binding equation is
\[
\sum_{m} t_{mn}(k) c_n = \epsilon c_m, \quad (1)
\]
where
\[
t_{mn}(k) = \begin{cases} t e^{-ik_{mn}} (r_m - r_n) & \text{for nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \quad (2)
\]
here \( m \) and \( n \) run over only the sites occupied by A-atoms. (The amplitudes on B-sites are zero in the split band limit.) Because each I-atom is surrounded by II-neighbors and vice versa, the above equations can also be written, for eigenvalue \( \epsilon = 0 \), as
\[
\sum_{m_I} t_{mn_I}(k) c_{n_I} = 0, \quad m_I = 1, ..., M_I, \quad (3)
\]
and
\[
\sum_{m_{II}} t_{mn_{II}}(k) c_{n_{II}} = 0, \quad m_{II} = 1, ..., M_{II}. \quad (4)
\]
Now there are \( M_I \) unknowns in the \( M_{II} \) homogeneous eq. (4). If the rank \( r \) of the matrix \( t_{mn} \) has the maximal value \( M_{II} \), then the eq. (4) have \( M_I - M_{II} \) independent solutions for the coefficients \( c_{n_I} \). In eq. (3) there are \( M_{II} \) unknowns and \( M_I \) eq. Because of the hermitian property of the matrix \( t_{mn} \), the rank of the matrix \( t_{mn_I} \) has then also the maximal value \( M_{II} \) and the eq. (3) have only the trivial solution
\[
c_{n_I} = 0. \quad (5)
\]
In this case, there are thus \( M_I - M_{II} \) independent solutions with finite amplitudes only on sublattice I. Some of these solutions correspond to isolated clusters of A atoms while others do not.

For a given value of \( v \) it is easy to calculate exactly the ensemble average for \( |M_I - M_{II}| \), which we denote by \( Z_1(v) \):
\[
Z_1(v) \equiv |M_I - M_{II}|_{av} = \sum_{M_I=0}^{v/2} \sum_{M_{II}=0}^{v/2} (M_I^{1/2} M_{II}^{1/2}) |M_I - M_{II}| \sim \sim (2 \pi)^{-1/2} v^{1/2}. \quad (6)
\]
If \( r < M_{II} \) the number of solutions \( Z(v) \) with zero eigenvalues exceeds \( |M_I - M_{II}| \). Thus, we have the rigorous inequality for the number of zero eigenvalues,
\[
Z(v) \geq Z_1(v) \sim (2 \pi)^{-1/2} v^{1/2}, \quad (7)
\]
which is to be compared with the total number of eigenvalues, \( v/2 \).

For very large \( v \) the fraction \( f_1(v) = Z_1(v)/(v/2) \) vanishes as \( v^{-1/2} \). However, there will be a contri-
bution, $Z_2(v)$, of zero eigenvalues from localized solutions (some, but not all, of which are contained in $Z_1$) which asymptotically is proportional to $v$. Thus, we also have the inequality $Z(v) \geq Z_2(v) \sim \alpha(v/2)$ where numerical estimates show that $\alpha$ is of the order 7 percent. (S. Kirkpatrick, T. P. Eggarter, to be published.)

In our computations with $v = 16$, 32, most of the zero-eigenvalues were due to the sublattice-effect embodied in $Z_1$. Here are our numerical results $f(v) = Z(v)/(v/2)$ compared to the calculated $f_1(v) = Z_1(v)/(v/2)$:

<table>
<thead>
<tr>
<th>$v$</th>
<th>$f(v)$ (numerical)</th>
<th>$f_1(v)$ (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.203</td>
<td>0.196</td>
</tr>
<tr>
<td>32</td>
<td>0.149</td>
<td>0.140</td>
</tr>
</tbody>
</table>

For a super-cell with $v$ odd, such as $v = 27$, the sublattice-effect does not exist, and our numerical value for the strength of the central peak, $f(v) = 0.067$, agrees well with those calculated by Kirkpatrick for $v = 1280$ and $3000 (0.080$ and $0.056)$. Our tentative conclusions are that, at least for this model and the split-band limit, numerical calculations with super-cells which divide into two sublattices are subject to an artificial error which vanishes only as $v^{-1/2}$. This problem does not arise for odd $v$, which appear to give good results for moderate values of $v$.

We wish to take this occasion to express our gratitude to Dr. C. Sommers and Professor Carl Moser of the Centre Européen de Calcul Atomique et Moléculaire for extensive help with the numerical calculations which made these additional comments possible.

References

[9] Veličky (B.), Kirkpatrick (S.) and Ehrenreich (H.), Phys. Rev., 1968, 175, 747. This paper includes a comprehensive review and critical analysis. We shall subsequently refer to this paper as VKE.