Energy gaps in disordered alloys

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The existence of an electronic energy gap is demonstrated for a three-dimensional model of a disordered binary alloy, assuming that one exists in both the pure materials. To do this, multiple scattering theory is applied to a model which has only s-wave scattering at each atomic site. A generalization to p-wave scattering is presented.

I. INTRODUCTION

The disordered binary alloy considered here is a crystal having N atomic sites, each of which can be occupied by either an A atom or a B atom. Thus 2^N cases are considered together. The extreme cases are the pure A crystal and the pure B crystal. To compute the electronic energy levels in these alloys, I assume that each electron moves in a potential which is the sum of contributions from each atom. If the potential wells centered at different atoms do not overlap, this model becomes a muffin-tin model. For such a model, Lloyd[1] has given a formal calculation of the electronic density of states; Lloyd and Smith[2] give a much more complete account. In the simplest form of this multiple scattering formalism, each atom is represented as a spherically symmetric scattering center, characterized by its phase shifts for each partial wave. Analytic treatment of the energy gaps in this muffin-tin alloy is difficult, but Taylor[3] and John[4] have given criteria for energy gaps. The present paper deals with a simplified model, having only s-wave scattering by each atom. Finitely many atoms are contained in a finite box of volume Ω, and periodic boundary conditions are used to avoid any appearance of surface states. Also, I assume that the atomic sites form a Bravais lattice. A theorem of Weyl[5] can be combined with the calculations of Lloyd and Smith, to produce the following result: If the energy E lies inside an energy gap in both the pure A crystal and the pure B crystal, then it does so in all 2^N cases. This result is proved below; it is a three-dimensional version of the early work of Saxon and Hutner[6] and Luttinger.[7] The same result is proved below for a model with p-wave scattering only and with atomic sites arranged in a simple cubic, body-centered cubic, or face-centered cubic lattice. Further generalization appears to be possible, and to be needed before these calculations can be compared with experiment.

The electronic energy levels appear as eigenvalues of a Hamiltonian

$$H = -\nabla^2 + V(\vec{r}) ,$$

where $\hbar = 1$ and the electronic mass is $\frac{1}{2}$. The potential $V(\vec{r})$ is a sum of contributions from all N atoms:

$$V(\vec{r}) = \sum v_A(|\vec{r} - \vec{R}_A|) + \sum v_B(|\vec{r} - \vec{R}_B|). \qquad (1)$$

Here the first sum is a sum over the A atoms, with centers at $\vec{R}_A$, and the second sum is a sum over the B atoms. The muffin-tin condition says that, for fixed $\vec{r}$, no more than one term in (1) is nonvanishing. Furthermore, the energy E is measured upward from the muffin-tin zero. Green's function is

$$G = (E - H)^{-1} . \qquad (2)$$

It depends on the numbers and arrangement of A and B atoms, as well as on E. Since N and Ω are finite, G is a meromorphic function of E. It can be exhibited in a rather explicit form if the potential $V(\vec{r})$ is turned off and the position representation is used. The free Green's function is

$$G_0(\vec{r}, \vec{r}') = \frac{1}{\Omega} \sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}}{E + i\epsilon - k^2} . \qquad (3)$$

Here the allowed values of $\vec{k}$ are determined by the periodic boundary conditions. The infinitesimal imaginary quantity in the denominator serves to make this the retarded Green's function, and the advanced Green's function could be obtained by a change of sign. This free Green's function appears in the Born series for (2). When terms of this series are to be evaluated for a muffin-tin model, it is useful to expand (3) in terms of spherical harmonics and spherical Bessel functions. The details need not be shown here; rather I shall use the notation of Lloyd and Smith.[2] Thus

$$\mathcal{G}_{LL'}(\vec{R}_\alpha, \vec{R}_{\alpha'}) \qquad (4)$$

is the propagator connecting atomic site α to atomic site α'. Note that L stands for both l and m, the two angular momentum quantum numbers. Scattering of waves at each atom is conveniently described by the single-site t matrix. This matrix is diagonal in L and α, with diagonal elements $t_{L\alpha}$; there is a requirement that (4) vanishes when $\alpha = \alpha'$. Summation of an infinite series gives Eq. (97) of Lloyd and

Smith, in which a matrix inversion appears explicitly. The matrix can be inverted if its determinant is not zero. Clearly zeros of the determinant are poles of (2). An interval on the real E axis in which no poles can occur, for any N, lies inside an energy gap; this criterion enables me to dispense with the limit $N \to \infty$. If $E<0$, the determinant of a finite Hermitian matrix is needed. I obtain the determinant by multiplying the eigenvalues together. Weyl's theorem gives an inequality for eigenvalues of a Hermitian matrix; see the Appendix. When all the eigenvalues are nonzero, the determinant does not vanish, and (2) cannot have a pole. This leads to an energy gap; the details of this argument are given in Sec. II.

If $E \geq 0$, the argument has to be modified somewhat. Instead of (3), the average of the advanced and retarded Green's functions is used. This average is expanded in spherical harmonics and spherical Bessel functions. $G^0_{LL'}(\vec{R}_\alpha, \vec{R}_{\alpha'})$ is the propagator connecting site α and site α'; it vanishes when $\alpha = \alpha'$. The properties of an atom are now described by a single-site reaction matrix, whose diagonal elements are $k_{L\alpha}$. Summation of the Born series gives Eq. (118) of Lloyd and Smith, in which a matrix inversion appears. The determinant of a Hermitian matrix is needed, and Weyl's theorem can again be applied. The details of this argument are given in Sec. III.

II. NEGATIVE ENERGIES

This section treats the simple problem of s-wave scattering with $E<0$, before considering the case of p waves. In the simple problem, $t_{L\alpha}=0$ if $l \neq 0$; hence $l=0$ in all spherical harmonics. Every spherical harmonic reduces to $(4\pi)^{-1/2}$, and (4) becomes

$$\mathcal{G}_{00}(\vec{R}_\alpha, \vec{R}_{\alpha'}) = \frac{4\pi}{\Omega} \sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{R}_\alpha - \vec{R}_{\alpha'})}}{E - k^2} \quad . \tag{5}$$

The single-site t matrix reduces to $t_{0\alpha}$, a number depending on α. Both (5) and $t_{0\alpha}$ are real because $E<0$, and the $i\epsilon$ is not needed in the denominator in (5). The poles of (2) are the zeros of the determinant of an $N \times N$ Hermitian matrix. Assuming that $t_{0\alpha}$ never vanishes, I may divide the αth row by $t_{0\alpha}$. The $\alpha\alpha'$ element of the resulting matrix is

$$\delta_{\alpha\alpha'}/t_{0\alpha} - \mathcal{G}_{00}(\vec{R}_\alpha, \vec{R}_{\alpha'}), \tag{6}$$

where $\delta_{\alpha\alpha'}$ is the Kronecker δ function. I note in passing that all eigenvalues of this matrix are nonzero if $|t_{0\alpha}|$ is sufficiently small; the gap theorem of Beeby and Edwards[8] can be proved in this way. In the present problem, the atomic sites form a Bravais lattice. Consequently, the matrix with elements (5) can be diagonalized by a Fourier transformation that removes the exponential function. If $t_{0\alpha}$ is independent of α, this transformation diagonalizes the matrix with elements (6), and each diagonal element is a 1×1 Korringa determinant.[9] In the present alloy problem $t_{0\alpha}$ is not independent of α, and the two terms in (6) represent matrices which cannot be diagonalized simultaneously. The first matrix has eigenvalues $1/t^{(A)}$ and $1/t^{(B)}$, corresponding to A and B atoms. The matrix with elements (5) has eigenvalues ranging from $g_{\min}$ to $g_{\max}$; below I prove that no part of this interval is free of eigenvalues. If the energy E lies in an energy gap of the pure A crystal,

$$1/t^{(A)} - g_{\max} < 1/t^{(A)} - g_{\min} < 0$$

or

$$1/t^{(A)} - g_{\min} > 1/t^{(A)} - g_{\max} > 0 \, .$$

Similarly, there are two alternative inequalities involving $1/t^{(B)}$. These inequalities can be combined with the inequalities in the Appendix, to show that all eigenvalues of the matrix with elements (6) are nonzero. Hence its determinant is not zero. If the energy interval considered lies in a gap in both the pure A and pure B cases, then the determinant must be nonzero throughout the interval, although (5) and $t_{0\alpha}$ depend on the energy. Therefore (2) cannot have any poles, and the energy gap exists in all 2^N cases.

This result depends on the eigenvalues of the matrix with elements (5). They range from $g_{\min}$ to $g_{\max}$, because they are bounded for all N. They effectively fill the interval from $g_{\min}$ to $g_{\max}$ when N and Ω are large. To show this, I write the eigenvalues of (5) as

$$\frac{4\pi N}{\Omega} \sum_{\vec{K}} \frac{1}{E - (\vec{k}+\vec{K})^2} - \frac{4\pi}{\Omega} \sum_{\vec{k}'} \frac{1}{E - k'^2} \quad , \tag{7}$$

where $\vec{k}$ labels the eigenvalue and $\vec{K}$ is a reciprocal-lattice vector. This difference of two divergent sums is defined as a limit of the difference; I require $|\vec{K}| < K_{\max}$ and $|\vec{k}'| < K_{\max}$, and I ask for the limit as $K_{\max} \to \infty$. This method of summation assures that (7) is a periodic function of $\vec{k}$. The sum converges uniformly in the first Brillouin zone, and it is bounded because $E<0$. I now consider continuous variation of $\vec{k}$, but not $\vec{k}'$. Then (7) becomes a bounded continuous periodic function of $\vec{k}$. It must take on all values from $g_{\min}$ to $g_{\max}$. In reality, $\vec{k}$ is limited to certain values because of the periodic boundary conditions; but when N and Ω are large, (7) comes close to every point in the interval from $g_{\min}$ to $g_{\max}$. This completes the proof, and completes the treatment of s-wave scattering.

The case of p-wave scattering only, when $E<0$, can be treated by a similar method. Since $t_{L\alpha}=0$ when $l \neq 1$, one keeps only terms with $l=1$; and each sum over L reduces to a sum over m, the magnetic quantum number. Note that $t_{L\alpha}$ is independent of m; it is equal to $t^{(A)}$ or $t^{(B)}$. I need the determinant of a $3N \times 3N$ Hermitian matrix, with elements

$$\frac{\delta_{LL'}\delta_{\alpha\alpha'}}{t_{L\alpha}} - \mathcal{G}_{LL'}(\vec{R}_\alpha, \vec{R}_{\alpha'}) \ .$$

This matrix is the sum of two Hermitian matrices. If the eigenvalues of the second matrix fill the range from $g_{\min}$ to $g_{\max}$, the theorem on energy gaps in alloys can be proved just as for s waves. Fourier transformation of the second matrix gives a 3×3 Hermitian matrix, in place of (7). If $\vec{k}$ is allowed to vary continuously, the three eigenvalues are bounded and continuous throughout the first Brillouin zone. The proof that they occupy only one interval along the real axis is straightforward for a simple cubic, body-centered cubic, or face-centered cubic Bravais lattice. Consider the case of $\vec{k}=0$. Each element of the 3×3 matrix is simply a sum over the lattice. Since $E<0$, there is a bound for this sum which is independent of Ω. According to Eqs. (92) and (93) of Lloyd and Smith, the sum involves spherical harmonics of the zeroth and second degree. The second-degree harmonics vanish when the sum over the lattice is performed; and the 3×3 matrix reduces to a multiple of the unit matrix. Therefore the three eigenvalues come together at $\vec{k}=0$. They must fill the interval from $g_{\min}$ to $g_{\max}$ as $\vec{k}$ varies continuously through the first Brillouin zone, which was to be proven.

III. NON-NEGATIVE ENERGIES

This section treats the case of s-wave scattering only, before going on to p-wave scattering. The energy satisfies $E\geq0$, and each Green's function is the average of advanced and retarded solutions. This prescription does not affect the location of poles of (2). In the case of s waves, the propagator from site to site is

$$G^0_{00}(\vec{R}_\alpha, \vec{R}_{\alpha'}). \tag{8}$$

The single-site reaction matrix is $k_{0\alpha}$, which is real and equal to either $k^{(A)}$ or $k^{(B)}$. The poles of (2) are the zeros of the determinant of an $N\times N$ matrix. Assuming that $k_{0\alpha}$ never vanishes, I divide the αth row by $k_{0\alpha}$. The result is a Hermitian matrix with elements

$$\delta_{\alpha\alpha'}/k_{0\alpha} - G^0_{00}(\vec{R}_\alpha, \vec{R}_{\alpha'}) \ . \tag{9}$$

If $k_{0\alpha}$ is independent of α, this matrix can be diagonalized by Fourier transformation, and the $\vec{k}$th diagonal element is a 1×1 Kohn-Rostoker determinant.[10] In the alloy case, at least the matrix with elements (8) can be diagonalized; and its eigenvalues must be studied. Since (8) is equal to the right-hand side of (5), the eigenvalues are given by (7). The denominators are strictly real, but vanishing denominators are quite possible.

However, the vanishing denominators in (7) cause no trouble. The periodic boundary conditions limit the possible values of $(\vec{k}+\vec{K})^2$ and k'^2. As E approaches one of these possible values, (7) approaches $\pm\infty$; only the ambiguous sign can depend on $\vec{k}$. Since $1/k^{(A)}$ and $1/k^{(B)}$ are bounded, all the eigenvalues of the matrix with elements (9) approach $\pm\infty$. The determinant cannot vanish, and these special values of E (which include $E=0$) need not be considered further.

The expression (7) can now be summed as above, and the sum is a periodic function of $\vec{k}$. The denominator

$$E-(\vec{k}+\vec{K})^2 \tag{10}$$

can become very small, but not when $|\vec{K}|$ is sufficiently large. If $|\vec{K}|\geq K_{\min}$, then (10) cannot vanish at any of the energies to be considered below when $\vec{k}$ is in the first Brillouin zone. The eigenvalue (7) can now be written

$$\frac{4\pi N}{\Omega}\sum_{\vec{K}}\frac{1}{E-(\vec{k}+\vec{K})^2}+R(\vec{k}) \ , \tag{11}$$

where the sum is restricted by the condition $|\vec{K}|<K_{\min}$. The remainder $R(\vec{k})$ is defined as the difference of two divergent sums, as in (7). It converges as $K_{\max}\to\infty$, and the convergence is uniform through the first Brillouin zone. If continuous variations of $\vec{k}$ are considered, $R(\vec{k})$ is a bounded continuous periodic function of $\vec{k}$, but the first term in (11) has a denominator which passes through zero. As $\vec{k}$ varies through the first Brillouin zone, (11) can approach $+\infty$ or $-\infty$, but it does not necessarily assume all real values. I want to prove that (11) has no more than one gap in its range of values. If this can be proved, then (11) is less than $g_{\max}$ or greater than $g_{\min}$. In this notation, $g_{\max}<g_{\min}$. Because of the periodic boundary conditions, $\vec{k}$ is limited to certain values and (11) is finite; but, when Ω is large, (11) can be much larger in absolute value than $|1/k^{(A)}|$. If the energy E lies in the gap of the pure A crystal, then

$$1/k^{(A)}-g_{\min}<0<1/k^{(A)}-g_{\max}$$

must hold. If it also lies in the energy gap of the pure B crystal, then $k^{(B)}$ satisfies a similar inequality. These two inequalities can be combined with the inequalities of the Appendix, to show that the matrix with elements (9) does not have zero eigenvalues. Therefore the determinant of this matrix cannot vanish. This result applies to all energies which lie in a gap for both pure A and pure B crystals, and it shows that these energies lie in a gap in all the 2^N alloy cases.

To complete the treatment of s-wave scattering, I have to show that the gap in the range of (11) is unique, if it exists. In this problem, $\vec{k}$ varies continuously through the first Brillouin zone, but the variation will be broken into small pieces. Consider a fixed straight path from the center to the edge of the first Brillouin zone, corresponding to a fixed direction for $\vec{k}$. The first term in (11)

gives rise to poles as k is varied. Each denominator in (11) is a quadratic function of k, with 0, 1, or 2 positive real zeros. These zeros give simple and double poles on the positive real k axis. Since the sum in (11) is finite, a finite number of poles will occur between the center and the edge of the first Brillouin zone, along the direction considered. Suppose that k_1 and k_2 are two consecutive poles. Then (11) is continuous for

$$k_1 < k < k_2 , \tag{12}$$

and it approaches $\pm\infty$ as $k \to k_1$, or $k \to k_2$. If (11) varies from $\pm\infty$ to $\mp\infty$, respectively, then it takes on all real values, there is no gap in its range, and there is nothing to prove. If (11) varies from $+\infty$ to $+\infty$ in the interval (12), then it reaches a minimum value, and does *not* assume values from this minimum down to $-\infty$. Similarly, if (11) varies from $-\infty$ to $-\infty$ in the interval (12), then it does not assume values from its maximum up to $+\infty$. In either case, (11) does not assume values lying in a semi-infinite interval. If $k_1 = 0$ or if k_2 corresponds to the edge of the first Brillouin zone, then the claim that (11) is unbounded at both k_1 and k_2 is not justified; but the conclusion about the interval (12) is unchanged. Consider now the whole path from center of edge of the first Brillouin zone. The set of values that (11) does not assume is the intersection of some semi-infinite intervals. More generally, consider all the straight paths from the center to the edge of the first Brillouin zone. They cover the whole Brillouin zone, and the gap in the range of (11) is the intersection of many semi-infinite intervals. This intersection may be the empty set, but it cannot consist of disjoint parts. This proves that the gap in the range of (11) is unique.

The problem of p-wave scattering at positive energies can be treated by an extension of this argument. In this problem, $l = 1$ everywhere, and the propagator $G^0_{LL'}(\vec{R}_\alpha, \vec{R}_{\alpha'})$ appears in place of (8). This number is an element of a $3N \times 3N$ Hermitian matrix, whose eigenvalues must be studied. Fourier transformation gives a 3×3 Hermitian matrix that depends on $\vec{k}$, a vector which I allow to vary continuously though the first Brillouin zone. In the simple cubic, body-centered cubic, and face-centered cubic lattices, a proof that each diagonal element of the 3×3 matrix is unbounded can be constructed, by adding together its values at the 48 different $\vec{k}$'s that are connected by the cubic symmetry. This result implies that at least one of the three eigenvalues is unbounded. If the three eigenvalues do not range over the entire real axis as $\vec{k}$ varies through the first Brillouin zone, I have to show that they leave only one gap. The variation of each eigenvalue as $\vec{k}$ varies can be followed, as in the previous paragraph. One of the eigenvalues is unbounded, and the real values which it does not assume, if any, constitute a single interval. The three eigenvalues come together at $\vec{k} = 0$; the proof of this is similar to that in Sec. II. Therefore the real values not assumed by any of the three eigenvalues make up a single interval, from $g_{\max}$ to $g_{\min}$. The gap theorem for alloys follows from this result, just as for s-wave scattering.

APPENDIX

Weyl[5] gives an inequality for the eigenvalues of Hermitian matrices, which is stated below. The inequality appears as Satz I in Weyl's paper, and is proved there.

Suppose that A and B are Hermitian matrices. Let the eigenvalues of A be

$$\alpha_1 \geq \alpha_2 \geq \alpha_3 \geq \cdots$$

and the eigenvalues of B be

$$\beta_1 \geq \beta_2 \geq \beta_3 \geq \cdots .$$

If the eigenvalues of $A + B$ are

$$\gamma_1 \geq \gamma_2 \geq \gamma_3 \geq \cdots ,$$

then, for any positive integers m and n,

$$\gamma_{m+n-1} \leq \alpha_m + \beta_n .$$

Furthermore, lower bounds for each eigenvalue of $A + B$ are obtained by reversing all the inequality signs that appear in this paragraph.

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[1]P. Lloyd, Proc. Phys. Soc. Lond. 90, 207 (1967).
[2]P. Lloyd and P. V. Smith, Adv. Phys. 21, 69 (1972).
[3]P. L. Taylor, Proc. Phys. Soc. Lond. 90, 233 (1967).
[4]W. John, Phys. Status Solidi B 49, K57 (1972).
[5]H. Weyl, Math. Ann. 71, 441 (1912).
[6]D. S. Saxon and R. A. Hutner, Phillips Res. Rep. 4, 81 (1949).
[7]J. M. Luttinger, Phillips Res. Rep. 6, 303 (1951).
[8]J. L. Beeby and S. F. Edwards, Proc. R. Soc. A 274, 395 (1963).
[9]J. Korringa, Physica 13, 392 (1947).
[10]W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).