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Density of states and random walks in semiconductor models III

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Abstract. The theory developed in two previous papers, for studying the Weaire model in terms of returning walks, is used here to study the density of electronic states at the band edges. The relationship between topological disorder and the shape of the band edges is considered and the shape of the inner band edge is shown to depend on oscillating terms in the asymptotic expansion of the number of returning walks. This work suggests the possibility of a band gap in a fourfold coordinated structure with $|V_1/V_2| > \frac{1}{2}$.

1. Introduction

In two previous papers (Lukes and Nix 1973a, b, to be referred to as I and II) a formalism is developed for studying the tight-binding hamiltonian of Weaire (1971) for both periodic and topologically disordered systems. Following II, the density of states per site of a W-fold coordinated structure is (quite generally)

$$n(E) = \frac{1}{\pi}\operatorname{Im}\left\{\frac{2(E^+ + V_1)}{(E^+ + V_1)^2 - V_2^2} + \frac{(2(E^+ + V_1) - WV_1)}{WV_1V_2}\sum_{t=0}^{n} c^{t+1}N(t)\right\} \tag{1.1}$$

where

$$c = \frac{V_1V_2}{(E^+ - (W-1)V_1)(E^+ + V_1) - V_2^2}$$

and $N(t)$ is the number of walks which return to the initial site after t steps.

It has been proved (Domb *et al* 1959) that the high-order moments of $n(E)$ and hence the asymptotic form of $N(t)$ determine the form of $n(E)$ near the upper band edge of a one-band model. The dependence of the lower band edge on the asymptotic form of the number of returning walks can be seen as follows: Domb *et al* have shown that by considering density of states with compact support in the positive energy region, the form of the upper band edge depends only on the higher moments of the density of states. For a one-band model with hamiltonian

$$H = V\sum_{(i,j)} |i\rangle\langle j|$$

the moments, μ_t, are $V^tN(t)$. Consider now a general density of states $n(E)$ with compact

support, which lies in both the positive and negative energy regions. This may be split into two terms

$$n(E) = n^{(1)}(E) + n^{(2)}(-E),$$

where

$$n^{(1)}(E) = n(E)\sigma(E)$$

$$n^{(2)}(E) = n(-E)\sigma(E),$$

and $\sigma(E)$ is the Heaviside step function.

The theorem of Domb *et al* can now be applied to both functions $n^{(1)}(E)$ and $n^{(2)}(E)$. The moment μ_t of $n(E)$ is related to the moments $\mu_t^{(1)}$ or $n^{(1)}(E)$ and $\mu_t^{(2)}$ of $n^{(2)}(E)$ by

$$\mu_t = \mu_t^{(1)} + (-1)^t \mu_t^{(2)},$$

where the asymptotic forms of $\mu_t^{(1)}$ and $\mu_t^{(2)}$ determine the nature of the upper and the lower band edges respectively. For positive V the order of magnitude of $\mu_t^{(1)}$ must be greater than or equal to the order of $\mu_t^{(2)}$. If the asymptotic form of μ_t is found to be

$$\mu_t \backsim a^t t^{-\nu_1} + (-b)^t t^{-\nu_2}, \tag{1.2}$$

then by an argument on orders of magnitude,

$$\mu_t^{(1)} \backsim a^t t^{-\nu_1} \qquad \text{and} \qquad \mu_t^{(2)} \backsim b^t t^{-\nu_2}.$$

It can now be seen that the behaviour of the lower band edge depends critically on the first term in the asymptotic expansion of the form $(-b)^t t^{-\nu_2}$. It is not possible to take $\mu_t^{(1)} > 0$ and $\mu_t^{(2)} = 0$ for the higher moments, for this would imply that the density of states is zero for negative energies.

Thorpe and Weaire (1971) have shown that the properties of the two-band Weaire model can be obtained from a one-band model. In their transformation, the upper and lower edges of the band in the one-band model correspond to the outer and inner edges of the bands in the two-band model. The above discussion of the one-band model can therefore be applied to the density of states at the edges of the band in the Weaire model. In papers I and II the density of states in the Weaire model at the outer band edges was considered. The purpose of the present paper is to extend the theory to deal with the inner band edges and then to speculate on the possible form of the density of states at these edges by looking at the first term which oscillates in sign in the asymptotic expansion of the number of returning walks for various examples.

2. Mathematical preliminaries

In order to calculate the density of states for some general asymptotic forms of $N(t)$ consider

$$I(a) = \sum_{t=n}^{\infty} a^{t+1} t^{-\nu} \tag{2.1}$$

with $\nu > 0$ and $n > 0$. A simple integral representation for $t^{-\nu}$ may be used to give

$$I(a) = \frac{1}{\Gamma(\nu)} \sum_{t=n}^{\infty} \int_0^{\infty} \mathrm{d}x\, a^{t+1}\, \mathrm{e}^{-tx} x^{\nu-1}. \tag{2.2}$$

The terms of the series $\Sigma_{t=n}^{\infty} a^t e^{-tx} x^{\nu-1}$ are continuous in x, and

$$|a^t e^{-tx} x^{\nu-1}| < |a|^t$$

for $t \geqslant n > (\nu-1)/e$ and $x \in (0, \infty)$. Thus the series is uniformly convergent in x for $|a| < 1$ and $x \in (0, \infty)$ and hence

$$\sum_{t=n}^{\infty} \int_0^{\infty} dx\, a^t e^{-tx} x^{\nu-1} = \int_0^{\infty} dx \sum_{t=n}^{\infty} a^t e^{-tx} x^{\nu-1}. \tag{2.3}$$

The sum inside the integral (2.3) is a geometric progression, and thus for $|a| < 1$ and $n > (\nu-1)/e$ it may be summed to give

$$I(a) = \frac{1}{\Gamma(\nu)} \int_0^{\infty} dx \frac{x^{\nu-1} a^{n+1} e^{-nx}}{1 - a e^{-x}}.$$

A simple change of variable puts the integral in the form

$$I(a) = \frac{a^{n+1}}{\Gamma(\nu)} \int_1^{\infty} dy \frac{(\ln y)^{\nu-1}}{y^n (y-a)} \qquad |a| < 1.$$

In this form $I(a)$ can be analytically continued to all complex values of a, apart from a cut running from 1 to ∞ along the real axis. The band edge therefore corresponds to $a = 1$. From (1.1) it is clear that to find the density of states it is necessary to consider in this general formalism

$$D(a, b) = \frac{1}{2\pi i} \lim_{\epsilon \to 0^+} [(b + i\epsilon) I(a + i\epsilon) - (b - i\epsilon) I(a - i\epsilon)].$$

In the limit this becomes

$$D(a, b) = \frac{ab}{\Gamma(\nu)} (\ln a)^{\nu-1} \sigma(a-1). \tag{2.4}$$

For a greater than but approximately equal to unity

$$D(a, b) = \frac{b(a-1)^{\nu-1}}{\Gamma(\nu)}.$$

The exponent $(\nu-1)$ agrees with that found by Domb *et al.*

The procedure developed above can be extended to incorporate a $\ln(t)$ term in the number of returning walks. Consider the series (2.1); by differentiating with respect to ν term by term the series becomes

$$-\sum_{t=n}^{\infty} a^{t+1} (\ln t) t^{-\nu}.$$

Thus for a series of this form the term corresponding to (2.4) will be

$$ab[\ln(\ln a) - \Gamma'(\nu)/\Gamma(\nu)] (\ln a)^{\nu-1} \sigma(a-1)/\Gamma(\nu),$$

and for $a \simeq 1$ this becomes

$$b(a-1)^{\nu-1} \ln(a-1) \sigma(a-1)/\Gamma(\nu).$$

3. Random walks and density of states for periodic lattices

The number of returning walks $N(t)$ for periodic lattices can be found in explicit form. The asymptotic forms of $N(t)$ for two periodic structures and the consequent shape of the band edges are investigated in this section in order that a better understanding of these be obtained.

In I the exact expression for the number of walks on a diamond lattice is substituted into the expression (1.1) for the density of states. The asymptotic form of $N(t)$ for a periodic diamond lattice is given by

$$N(t) = \begin{cases} 2\left(\frac{2}{\pi t}\right)^{3/2}(4)^t & t \text{ even} \\ 0 & t \text{ odd.} \end{cases} \tag{3.1}$$

The density of states at the band edges is then determined by the series

$$\frac{1}{2^{3/2}} \sum_{t=n}^{\infty} (16c^2)^t t^{-3/2}. \tag{3.2}$$

From § 2 it can be seen that the band edges occur at $16c^2 = 1$. Equation (3.2) can be rewritten as

$$\frac{1}{2}\left(\sum_{t=2n}^{\infty} (4c)^t t^{-3/2} + \sum_{t=2n}^{\infty} (-4c)^t t^{-3/2} \right). \tag{3.3}$$

This form implies that the outer band edges occur at $4c = 1$ and the inner band edges at $4c = -1$. The function c appears in (1.1) and for $W = 4$ a graph is shown in figure 1. The band edges are found to occur at

$$c = \tfrac{1}{4} \qquad E = 3V_1 + V_2 \qquad \text{or} \qquad E = -V_1 - V_2$$
$$c = -\tfrac{1}{4} \qquad E = -V_1 + V_2 \qquad \text{or} \qquad E = 3V_1 - V_2.$$

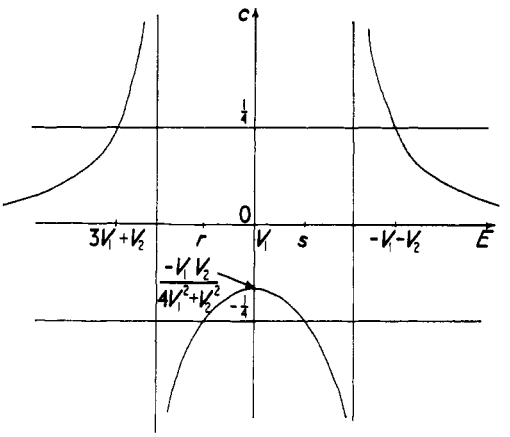

Figure 1. Graph of E against c (for $2V_1/V_2 > 1$ the points r, s are $-V_1 + V_2$, $3V_1 - V_2$ respectively and for $2V_1/V_2 < 1$, $3V_1 - V_2$, $-V_1 + V_2$ respectively).

From the general formula of § 2, with $a = 4c$ and $b = 2(E-V_1)/4V_1V_2$, the density of states per site at the band edges becomes

$$n(E) = \frac{2}{\pi^2}\left|\frac{2V_1+V_2}{V_1V_2}\right|^{3/2}|\Delta E|^{1/2}$$

at the outer band edges and

$$n(E) = \frac{2}{\pi^2}\left|\frac{2V_1-V_2}{V_1V_2}\right|^{3/2}|\Delta E|^{1/2}$$

at the inner band edges where ΔE is the energy measured into the band relative to the band edge.

Because the model is reformulated in II in terms of general coordination number, it is possible to consider other lattices. A lattice which proves important as far as this discussion is concerned, but which is not a likely structure for a semiconductor, is the face-centred cubic lattice. This has twelvefold coordination; the number of returning walks is given by

$$N(t) = \frac{(12)^t}{\pi^3}\int_0^{\pi}\int\int \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\left(\frac{\cos x\cos y+\cos x\cos z+\cos y\cos z}{3}\right)^t.$$

The series which appears in the density of states may be summed as a geometric progression to give

$$\sum c^t N(t) = \frac{1}{\pi^3}\int_0^{\pi}\int\int \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,[1-4c(\cos x\cos y+\cos y\cos z+\cos z\cos x)]^{-1}.$$

The denominator varies from $1-12c$ to $1+4c$ and hence there are branch points at $c = \frac{1}{12}$ and $c = -\frac{1}{4}$. This is in contrast to the diamond lattice, the simple-cubic lattice and several others which have branch points at $c = \pm 1/W$. The asymptotic form for the number of walks on a face-centred cubic lattice can be shown by a saddle-point approximation to be of the form

$$N(t) = \frac{1}{4}\left(\frac{3}{\pi t}\right)^{3/2}(12)^t + \frac{3(-4)^t}{2\pi^2 t}\ln t$$

where only the leading term which alternates in sign is retained. It is to be noted that constant coefficients of each term depend on the multiplicities of the extremum values. The density of states at the outer band edges can then be expected to vary as $|\Delta E|^{1/2}$ and at the inner band edges as $-\ln|\Delta E|$. The infinite density of states at the inner band edges can be thought of physically as an accumulation of states at the band edges due to the fact that the band edges in this example do not occur symmetrically, that is $Wc \neq \pm 1$. The fact that the singularity is logarithmic arises from the peculiar dispersion law for an electron moving on the square face of the Brillouin zone.

4. Density of states and topological disorder

In order to introduce topological disorder it is instructive to consider a random walk in three dimensions such that the individual steps are of constant length l, but in random

directions. The probability density of a return to the origin after t steps is given by (Rayleigh 1919)

$$P_t(\mathbf{0}) = \frac{1}{4\pi^2 l^3}\int_{-\infty}^{\infty} dx\, x^2 \left(\frac{\sin x}{x}\right)^t. \tag{4.1}$$

For large t a saddle-point approximation can be made. This leads to an expansion of $\sin x/x$ about its extrema. It has extrema at $x = 0, \pm 4{\cdot}5, \pm 7{\cdot}7$, etc, of which previous authors only use the central one. The contributions from the first three central values gives

$$P_t(\mathbf{0}) = \frac{3\sqrt{6}}{4l^3(\pi t)^{3/2}} + \frac{2{\cdot}56}{l^3 t^{1/2}}(-0{\cdot}22)^t, \tag{4.2}$$

which is of the desired form for determining the behaviour at the inner band edges. From (4.2) the leading term in $N(t)$ can be seen to be proportional to $W^t t^{-3/2}$, where again W is the coordination number. It thus appears that in any returning walks, on a lattice or completely random, the leading term in the asymptotic form of the number of walks contains a factor $t^{-3/2}$. This would mean that the density of states at the outer edges, in the Weaire model, would behave as $(\Delta E)^{1/2}$ in the crystalline and disordered case. If not all the bonds are saturated, that is there is some average coordination number $\overline{W} < W$, the leading term in the number of walks would be expected to be proportional to $(\overline{W})^t t^{-3/2}$. This would result in a shift of the position of the outer band edges but not a change in shape.

The various examples suggest that the number of walks function for a disordered solid should be of the form

$$N(t) = \frac{A(f)^t}{t^{3/2}} + \frac{B(-g)^t}{t^v} \tag{4.3}$$

with $\frac{1}{2} \leqslant v \leqslant \frac{3}{2}$ and $0 < f \leqslant W$, $0 < g \leqslant W$.

There is also the possibility of dealing with a $\ln(t)$ in the second term. Upon substituting this form for $N(t)$ into the expression (1.1) for the density of states, and using the theory developed in § 2, it can be seen that the band edges occur at $fc = 1$ and $gc = 1$. This shows that the band edges are only symmetrical if $f = g$ in which case $v \geqslant \frac{3}{2}$. It may thus be expected that $g \leqslant f$. The behaviour of the density of states at the inner band edges could then be expected to vary between $(\Delta E)^{-1/2}$ and $(\Delta E)^{1/2}$.

The first term in (1.1) gives delta functions in the density of states at energies $E = -V_1 \pm V_2$. It is to be noted that the position of these delta functions is independent of the coordination number, and the asymptotic form of the number of walks function. For a diamond lattice with $|V_1/V_2| > \frac{1}{2}$ one delta function is positioned on the lower edge of the upper band. However, for a face-centred cubic lattice or for a topologically disordered lattice it has been shown that there could be a shift of the inner band edges causing a gap to appear. Thus, for a general coordination number and for topologically disordered systems, there could possibly be a gap between the occupied and unoccupied states for $|V_1/V_2| > 2/W$ as well as for $|V_1/V_2| < 2/W$.

In conclusion it has been shown that the formalism previously developed together with application to specific examples suggest some limits on the positions of the band edges and the shape of the density of states at these edges. It is to be noted that the nature of the inner band edges depends critically on the first term which oscillates in sign in the asymptotic expansion of the number of walks which return to the origin.

Further knowledge of this function for amorphous systems is necessary before any definite conclusions can be drawn about the nature of the electron spectrum for real amorphous systems.

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