

Energy band structure of a two-dimensional liquid with nearest-neighbour angular correlations

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MS. received 5th December 1966, in revised form 20th March 1967

Abstract. The electronic energy bands of a two-dimensional liquid in which there are angular correlations between the positions of nearest-neighbour atoms are investigated, using an extension of the Greenian formalism of Phariseau and Ziman and a generalized coherent-wave approximation. Near $\mathbf{k} = 0$, and when the number of nearest neighbours is odd, it is found that, in addition to the normal bands in which the wave function has the same sign on each atom, bands occur in which the wave function is essentially of opposite sign on nearest-neighbour atoms. The energy bands in such liquids therefore closely resemble those in the corresponding crystal having two atoms per unit cell. In particular, different band edges can be identified with wave functions possessing bonding or antibonding properties.

As the degree of angular correlation is decreased, the imaginary part of the wave vector or energy in these new bands increases and the bands ultimately disappear as the nearest-neighbour environment approaches spherical symmetry. The energy states associated with these bands presumably become added to the symmetric-sign bands as states of large wave vector.

The extension of these findings to three dimensions is conjectured and the results are applied briefly to a discussion of the energy band structure of amorphous germanium, which is a semiconductor, and of liquid germanium, which is a metal.

1. Introduction

In the usual discussions of the electronic structure of solids the existence of energy bands and band gaps is closely related to the existence of long-range atomic order. It may therefore be expected that the magnitude, or even the existence, of these band gaps will be greatly affected by a transition to the liquid state in which all long-range order is lost.

For materials which are metals in the solid state the effect of such changes upon their electrical properties may not be large, because the Fermi surface is not very close to a band edge over much of its area. In the case of semiconductors, however, the effect of melting can be very great. Thus crystalline germanium, for example, is a semiconductor with an energy gap of 0.7 eV while liquid germanium is a metal.

Not all semiconductors behave in this way. Some remain semiconducting in the liquid state. In addition, it is possible to prepare specimens of some materials in an amorphous solid state in which they also behave as semiconductors. Germanium is particularly interesting in this connection since it can exist in an amorphous semiconducting state as well as in the crystalline and metallic liquid states mentioned above.

The optical properties of amorphous germanium, prepared by vacuum evaporation onto a cold substrate, have been extensively studied by Tauc *et al.* (1966) who concluded that its band structure near $\mathbf{k} = 0$ is very similar to that of crystalline germanium. On the other hand, x-ray diffraction data (Richter and Breitling 1958) suggest that, whilst each atom is surrounded approximately tetrahedrally by four others, neighbouring tetrahedra are free to rotate about their common bond so that quasi-crystalline order does not extend much past nearest neighbours. Liquid germanium, while still retaining an average co-ordination number of 4 to 5, does not appear to have so much nearest-neighbour angular ordering.

These observations lead to the assumption that, in germanium at any rate, the existence of the band gap, and hence of semiconducting properties, is determined largely by the short-range, rather than the long-range, order. The existence of similar bonding structures in

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materials like selenium which remain semiconducting in the amorphous state suggest that this principle may be of rather general applicability.

Theories of the electrical properties of amorphous materials based on this principle have been developed by workers of the Russian school (Gubanov 1965, Moorjani and Feldman 1964) who treat the amorphous solid as derived from a distorted crystal lattice. This procedure, however, imposes wave functions on the system to some extent and it is not obvious that all relevant amorphous structures can be obtained in a convergent way by this means.

It is therefore desirable to show that the bonding and antibonding wave functions which are characteristic of a semiconducting crystal can be obtained in a consistent way from the sort of formalism generally used in the treatment of liquid metals. To do this we shall require to generalize this formalism to take account of angular correlations between nearest-neighbour atoms, since this appears to be at the core of the distinction between semiconducting and metallic states.

Since angular correlations have no meaning in one dimension and since the three-dimensional case is rather complicated, we shall present the development in terms of a two-dimensional system. In this way the fundamental ideas are not obscured by algebraic complexity, while the essential features of the physical situation still emerge.

2. Integral equation formulation

The treatment we shall use is based on that developed for crystalline solids by Korringa (1947), by Kohn and Rostoker (1954) and later by Segall (1957) and by Ham and Segall (1961). It was applied in modified form to simple liquids by Phariseau and Ziman (1963) and a recent more general discussion has been given by Ziman (1966). This method has the prime advantage that the formalism is closely related to the physics involved—the scattering of an electron wave from an array of spherical obstacles—so that the implicit assumptions made are readily apparent. There is also a close formal connection between this approach and the more familiar augmented plane-wave method (Morgan 1966).

We seek solutions of the Schrödinger equation which, in appropriate units, may be written

$$\{-\nabla^2 + V(\mathbf{r})\}\psi(\mathbf{r}) = \kappa^2\psi(\mathbf{r}) \quad (1)$$

where $V(\mathbf{r})$ is a self-consistent potential for the complete array of atoms and κ is related to the energy E by $\kappa^2 = E$.

This equation is equivalent to the integral equation

$$\psi(\mathbf{r}) = \int \mathcal{G}_0(\mathbf{r}-\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}') d\mathbf{r}' \quad (2)$$

where \mathcal{G}_0 is the free-space propagator or Green function, which satisfies

$$\{\nabla^2 + \kappa^2\}\mathcal{G}_0(\mathbf{r}-\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \quad (3)$$

and which has, in two dimensions, the explicit form

$$\mathcal{G}_0(\mathbf{r}-\mathbf{r}') = -\frac{i}{4}H_0^{(1)}(\kappa|\mathbf{r}-\mathbf{r}'|) \quad (4)$$

where $H_0^{(1)}(z)$ is the Hankel function of the first kind and of order zero, defined by

$$H_0^{(1)}(z) = J_0(z) + iN_0(z). \quad (5)$$

To make further progress it is necessary to assume that, by appropriate choice of energy zero, $V(\mathbf{r})$ can be adequately approximated by a 'muffin-tin potential' which has circular symmetry within a set of non-overlapping circles of radius r_s centred upon the atomic positions \mathbf{x}_j and is zero elsewhere. Choosing new coordinates $\boldsymbol{\rho}$ relative to the positions of the atomic centres such that

$$\mathbf{r} = \mathbf{x}_j + \boldsymbol{\rho} \quad (6)$$

and writing

$$\psi(\mathbf{r}) = \psi_j(\boldsymbol{\rho}); \quad V(\mathbf{r}) = v(\rho) \quad (7)$$

within the atomic circle centred upon \mathbf{x}_j , (2) becomes

$$\psi_j(\boldsymbol{\rho}) = \sum_j \int \mathcal{G}_0(\boldsymbol{\rho} - \boldsymbol{\rho}' + \mathbf{x}_j - \mathbf{x}_{j'}) v(\boldsymbol{\rho}') \psi_{j'}(\boldsymbol{\rho}') d\boldsymbol{\rho}'. \quad (8)$$

3. Coherent-wave approximation

In the case of a crystalline solid, (8) can be immediately simplified by using the Bloch theorem to write

$$\psi_j(\boldsymbol{\rho}) = \exp(i\mathbf{k} \cdot \mathbf{x}_j) \psi_0(\boldsymbol{\rho}) \quad (9)$$

where $\psi_0(\boldsymbol{\rho})$ is the wave function in the cell at the origin. Because of the 'muffin-tin' nature of $v(\boldsymbol{\rho})$, (8) can then be reduced to an integration over a single atomic circle together with a summation which can be expressed as

$$G(\boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_j \mathcal{G}_0(\boldsymbol{\rho} - \boldsymbol{\rho}' - \mathbf{x}_j) \exp(i\mathbf{k} \cdot \mathbf{x}_j). \quad (10)$$

$G(\boldsymbol{\rho}, \boldsymbol{\rho}')$ has been called the Greenian of the system.

If the crystal has more than one atom per unit cell, then (9) is generalized to

$$\psi_j^{(i)} = \exp(i\mathbf{k} \cdot \mathbf{x}_j) \psi_0^{(i)} \quad (11)$$

where the index i runs over the atoms of the cell.

The basic assumption of the Phariseau-Ziman method is that one can introduce a coherent-wave approximation of the same form as the Bloch relation (9) to relate the ensemble average wave function on one atom to that on another. The exact nature of the physical and mathematical approximations involved in this assumption has not yet been fully investigated, though Ziman (1966) has discussed some of the formal assumptions implied, and the relation of the solution to that given by an expansion of the Green function has been considered by Ballentine and Heine (1964). We shall adopt a generalized form of this coherent-wave approximation, in a sense to be discussed below, in the present development, with the general interpretation that the coherent wave is only part of the total wave function and that the propagation vector \mathbf{k} , which is now complex, represents a propagating wave which is attenuated by scattering.

We are interested in a situation in which the two-dimensional liquid has a short-range order in the sense that each atom tends to have Z nearest neighbours arranged symmetrically about it. These Z atoms will not generally be all at exactly the same distance, nor will their angular arrangement be perfect. Nevertheless, provided the deviations are not too great, it will be possible to define an angular orientation α of the nearest-neighbour environment relative to some standard orientation, as illustrated in figure 1. As the deviations become greater, this will involve making a least-squares best fit and ultimately, for complete disorder, it may no longer be possible. We shall see later that this failure for large disorder is an integral part of the theory.

Now, instead of performing a complete ensemble average over all atoms of the liquid, we recognize that the index α should be preserved by analogy with the index i in (11). Since α is a continuous variable, we take a small range of orientations $d\alpha$ and perform an ensemble average over all atoms belonging to this set. The ensemble average so defined has a definite nearest-neighbour orientation and those neighbours have angular positions defined by the bonds of the orientation, except that each bond angle has a Gaussian distribution of half-width δ about its mean value. This situation is illustrated in figure 1. The distribution of more distant atoms is essentially circularly symmetric though we could easily include angular correlations of more distant neighbours if we wished. The radial distribution of nearest neighbours is specified by a radial function $g_1(r)$ and that of more distant atoms by $g_2(r)$, where these quantities are defined so that the number of atoms lying between circles of radii r and $r + dr$ is $Ng_i(r) dr$. N is the average number density of atoms in the liquid and the total radial distribution function is

$$g(r) = g_1(r) + g_2(r). \quad (12)$$

After this partial ensemble average has been taken, the atoms of the liquid all have identical

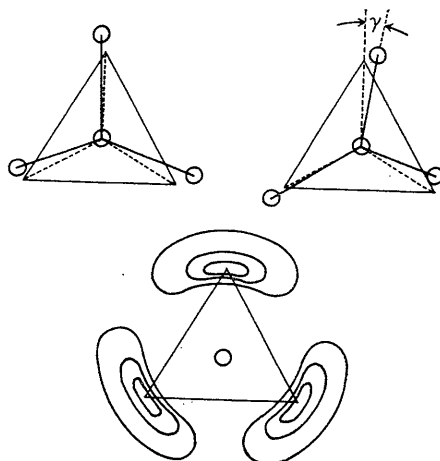


Figure 1. Two different atoms in a liquid with co-ordination number $Z = 3$ having the same orientation α , as indicated by the triangle, but differing in bond angle displacements γ and in nearest-neighbour distances. The third figure shows contours of the ensemble average environment for this orientation α .

environments in terms of the radial functions $g_i(r)$ and differ from each other only through the orientation α of their angular environments.

As an appropriate generalization of the crystalline relation (11) we now assume a generalized coherent-wave approximation of the form

$$\psi_j^{\alpha'} = \exp(i\mathbf{k} \cdot \mathbf{x}_j) \mathcal{R}(\alpha' - \alpha) \psi_0^\alpha \quad (13)$$

where α is the orientation of the environment of the atom at the origin and the operator $\mathcal{R}(\alpha' - \alpha)$ is as yet undetermined.

To determine the form of $\mathcal{R}(\alpha)$ we note that it is, in general, a function of \mathbf{k} and may depend on other quantum numbers as well, so that it may not produce the same effect on all states of the same \mathbf{k} . However, if Z is the number of nearest neighbours, we must have

$$\mathcal{R}(2s\pi/Z) = 1, \quad s = 0, 1, 2, \dots \quad (14)$$

and also, for this two-dimensional case,

$$\mathcal{R}(\alpha)\mathcal{R}(\beta) = \mathcal{R}(\beta)\mathcal{R}(\alpha) = \mathcal{R}(\alpha + \beta). \quad (15)$$

To evaluate $\mathcal{R}(\alpha)$ more specifically we note that, if the wave functions ψ on the atoms of our problem are expanded in terms of a set of orthonormal functions u_m , then $\mathcal{R}(\alpha)$ is an operator in the space of the u_m and, from (14), an appropriate expansion is given by the matrix elements

$$\mathcal{R}_{mm'}(\alpha) = \sum_n a_{n,mm'} \exp(inZ\alpha) \quad (16)$$

with $n = 0, 1, 2, \dots$. Since all rotations in two dimensions commute, as in (15), it is possible to select the set u_m so as to simultaneously diagonalize all the $\mathcal{R}_{mm'}$ so that we have the expansion

$$\mathcal{R}_{mm'}(\alpha) = \sum_n a_{nm} \delta_{mm'} \exp(inZ\alpha). \quad (17)$$

The matrix coefficients a_{nm} are, in general, functions of \mathbf{k} .

This expansion is general enough to describe all possible properties of $\mathcal{R}(\alpha)$ in the two-dimensional case.† It also represents a possible, though unnecessarily complicated,

† In an earlier publication (Fletcher 1967) and using a more restricted physical model it was assumed that, very near $\mathbf{k} = 0$, $\mathcal{R}(\alpha)$ can be represented to a first approximation by a simple rotation through α . While this assumption leads to no inconsistencies for the model considered, the present development is more general and supersedes that given in this reference.

starting point for the treatment by the Kohn-Rostoker method of a crystal with several identical atoms per unit cell.

4. Greenian formalism

If we substitute the generalized coherent-wave approximation (13) into the integral equation (8), take $\mathbf{x}_j = 0$ and then replace j' by j , we obtain

$$\mathcal{R}(\alpha)\psi_0^0(\rho) = \int \sum_j \mathcal{G}_0(\rho - \rho' - \mathbf{x}_j) \exp(i\mathbf{k} \cdot \mathbf{x}_j) \mathcal{R}(\alpha_j) v(\rho') \psi_0^0(\rho') d\rho' \quad (18)$$

where $\psi_0^0(\rho)$ is the wave function in a circular cell of standard orientation $\alpha = 0$, α is the orientation of the cell at the origin, and the integration now extends over only a single cell.

The Greenian operator for the system now has the form

$$G^\alpha(\rho, \rho') = \langle \sum_j \mathcal{G}_0(\rho - \rho' - \mathbf{x}_j) \exp(i\mathbf{k} \cdot \mathbf{x}_j) \mathcal{R}(\alpha_j) \dots \rangle \quad (19)$$

where the wave function and potential on which G^α operates are the subject of this operation before the configurational average, indicated by $\langle \rangle$, is taken. This average does not include an average over the orientation of the cell at the origin, so G^α still depends upon α formally in the same way as it would depend upon the index i of equation (11) in a crystal with more than one atom per cell. The ensemble average over directions in the liquid essentially rotates the reference orientation $\alpha = 0$ along with the cell orientations α_j . The most appropriate procedure is therefore to average over directions of the propagation vector \mathbf{k} in (19) and this may be taken to be implied in $\langle \rangle$. This Greenian contains all structural information about the system, while information about the atomic potentials is separated into $v(\rho)$ and the behaviour of $\psi(\rho)$ within an atomic circle.

On the basis of our discussion above we can now decompose G^α into three terms, representing the atom at the origin, its nearest neighbours and further atoms respectively, as follows:

$$G^\alpha(\rho, \rho') = \mathcal{G}_0(\rho - \rho') \mathcal{R}(\alpha) + G_1^\alpha(\rho, \rho') + G_2^\alpha(\rho, \rho') \quad (20)$$

where

$$G_1^\alpha(\rho, \rho') = \left\langle \frac{N}{Z} \sum_j \int \mathcal{G}_0(\rho - \rho' - \mathbf{x}_j) \exp(i\mathbf{k} \cdot \mathbf{x}_j) g_1(x_j) dx_j \mathcal{R}(\alpha_j) \dots \right\rangle_1 \quad (21)$$

and

$$G_2^\alpha(\rho, \rho') = \left\langle \frac{N}{2\pi} \int \int \mathcal{G}_0(\rho - \rho' - \mathbf{x}) \exp(i\mathbf{k} \cdot \mathbf{x}) g_2(x) dx d\Omega(\mathbf{x}) \mathcal{R}(\alpha) \dots \right\rangle_2 \quad (22)$$

The ensemble averages in (21) and (22) are those appropriate to the orientations of nearest neighbours and non-nearest neighbours respectively, and over all directions of \mathbf{k} .

5. Variational procedure

The method of Kohn and Rostoker now proceeds by establishing that the integral equation (2) is equivalent to the variational principle

$$\delta\Lambda = 0 \quad (23)$$

where Λ is the functional

$$\Lambda = \int \psi^*(\mathbf{r}) V(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} - \iint \psi^*(\mathbf{r}) V(\mathbf{r}) \mathcal{G}_0(\mathbf{r} - \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \quad (24)$$

and all variations $\delta\psi$ are allowed, including those which do not satisfy the boundary conditions.

Since, under the assumption of a muffin-tin potential, the Hamiltonian for an individual atomic cell commutes with the operators $\mathcal{R}(\alpha)$, it is possible to select a set of basis functions which simultaneously diagonalize the Hamiltonian and the operators $\mathcal{R}(\alpha)$. There is no ambiguity about the choice of these basis functions and the appropriate expansion of the

wave function $\psi(\rho)$ within one of the circularly symmetrical potential regions is

$$\psi(\rho) = \sum_m b_m R_m(\rho) \exp(im\phi) \tag{25}$$

where the b_m are constants and the $R_m(\rho)$ are solutions of the radial Schrödinger equation.

From the explicit form (17) for $\mathcal{R}(\alpha)$ we can now evaluate the effect of its operation on $\psi(\rho)$. Because of the $\delta_{mm'}$ in (17), the coefficients a_{nm} and $b_{m'}$ always occur in the combination $a_{nm}b_{m'}$ and we can replace this by a single symbol

$$\beta_{nm} \equiv a_{nm}b_{m'}. \tag{26}$$

These coefficients β_{nm} are the quantities which are to be varied in (23).

We could proceed from (23) but an identical equation is arrived at (Kohn and Rostoker 1954, Ziman 1966) if we apply instead the condition

$$\int \left[G^\alpha(\rho, \rho') \left\{ \frac{\partial}{\partial \rho'} \psi(\rho') \right\} - \left\{ \frac{\partial}{\partial \rho'} G^\alpha(\rho, \rho') \right\} \psi(\rho') \right]_{\rho' = r_s - \epsilon} d\phi(\rho') \tag{27}$$

where $G^\alpha(\rho, \rho')$ is the Greenian operator given by (20), r_s is the radius of the atomic circles, ϵ is an infinitesimal positive quantity and $\rho < \rho'$. It turns out, as we shall see later, that (27) provides a set of only M equations, where M is the number of m values included in the expansion (25), while there are $M \times N$ independent coefficients β_{mn} , where N is the number of n values included in (16). We can, however, derive just the required number of independent equations from (27) by considering this equation for N different values of the orientation α . This procedure, as we shall show later, is quite unique.

From here we follow closely the two-dimensional analogue of the development of Kohn and Rostoker or of Phariseau and Ziman and for that reason we sketch it in outline only.

The free-space propagator given by (4) can be expanded (Watson 1944) as

$$\mathcal{G}_0(\rho - \rho') = -\frac{i}{4} \sum_{m=-\infty}^{\infty} J_m(\kappa\rho) H_m^{(1)}(\kappa\rho') \exp\{im\phi(\rho)\} \exp\{-im\phi(\rho')\} \tag{28}$$

for $\rho < \rho'$. Since the G_i^α of (20) are non-singular, we can find for them similar expansions of the form

$$G_i^\alpha(\rho, \rho') = -\frac{i}{4} \sum_{m,m'=-\infty}^{\infty} \mathcal{B}_{mm'}^{\alpha,i} J_m(\kappa\rho) J_{m'}(\kappa\rho') \exp\{im\phi(\rho)\} \exp\{-im'\phi(\rho')\} \tag{29}$$

where the $\mathcal{B}_{mm'}^{\alpha,i}$ have now to be determined. To do this we use the two-dimensional plane-wave expansion

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = \sum_m i^m J_m(\kappa r) \exp\{im\phi(\mathbf{r})\} \exp\{-im\phi(\mathbf{k})\} \tag{30}$$

from which we derive

$$J_m(\kappa R) \exp\{im\phi(\mathbf{R})\} = \sum_{m'} J_{m'}(\kappa\rho) J_{m'-m}(\kappa\rho') \exp\{im'\phi(\rho)\} \exp\{i(m-m')\phi(\rho')\} \tag{31}$$

where

$$\mathbf{R} = \rho - \rho'. \tag{32}$$

This gives

$$\begin{aligned} \mathcal{G}_0(\rho - \rho' - \mathbf{x}) &= -\frac{i}{4} \sum_{mm'} H_m^{(1)}(\kappa x) \exp\{-im\phi(\mathbf{x})\} \\ &\quad \times J_{m'}(\kappa\rho) J_{m'-m}(\kappa\rho') \exp\{im'\phi(\rho)\} \exp\{i(m'-m)\phi(\rho')\} \end{aligned} \tag{33}$$

which leads finally to

$$\mathcal{B}_{mm'}^{\alpha,1} = \frac{1}{Z} A_{0,m-m'}^{(1)} \sum_j \exp\{i(m'-m)\bar{\phi}(\mathbf{x}_j)\} \langle \mathcal{R}(\alpha) \rangle_1 \tag{34}$$

$$\mathcal{B}_{mm'}^{\alpha,2} = A_{0,0}^{(2)} \langle \mathcal{R}(\alpha) \rangle_2 \delta_{mm'} \tag{35}$$

where the ensemble averages are over the orientations of nearest neighbours or of more

distant atoms respectively and

$$A_{m,m'}^{(i)} = N \int_0^\infty J_m(kx) H_{m'}^{(1)}(\kappa x) g_i(x) dx. \quad (36)$$

We can further simplify (34) by noting that for Z symmetrically disposed nearest neighbours, which is what is implied by the ensemble average $\bar{\phi}(\mathbf{x}_j)$,

$$\bar{\phi}(\mathbf{x}_j) = \phi_0 + 2\pi j/Z, \quad j = 1, 2, 3, \dots, Z \quad (37)$$

where ϕ_0 is a constant. Thus, unless $|m' - m| = nZ$ with $n = 1, 2, \dots$, (34) becomes

$$\mathcal{B}_{mm'}^{\alpha,1} = A_{0,0}^{(1)} \langle \mathcal{R}(\alpha) \rangle_1 \delta_{mm'}. \quad (38)$$

In the cases we shall be considering, $Z \geq 3$ while m, m' will be 0 or 1 so that (38) will always be valid, though this will no longer be the case if higher momenta m are included.

When we substitute the Greenian operator $G(\rho, \rho')$ as defined by (20), (28), (29), (35) and (38), into (27), we are led to consider the effects of the operators $\langle \mathcal{R}(\alpha) \rangle_1$ and $\langle \mathcal{R}(\alpha) \rangle_2$ upon the angular parts of the wave function $\psi(\rho')$ defined by (25) and (26). Two distinct cases arise, depending upon whether the co-ordination number Z is even or odd.

5.1. Odd co-ordination number

Let us consider the case when Z is odd and suppose that the regular Z -fold symmetry of a given atom is distorted in such a way that any bond may vary from its symmetrical position by an angle γ as shown in figure 1. γ is distributed in some manner such as $(1/\delta\sqrt{\pi}) \exp(-\gamma^2/4\delta^2)$, where δ specifies the half-width of the distribution.

Now for nearest neighbours the difference in average orientation, $\alpha - \alpha_0$, is necessarily π/Z but this can vary slightly because of the distortions γ . Noting the decomposition of $\mathcal{R}(\alpha)$ given by (17), we see that for nearest neighbours

$$\begin{aligned} \langle \exp(inZ\alpha) \rangle_1 \exp(im\phi) &= \frac{2}{\delta\sqrt{\pi}} \int_{-\infty}^{\infty} \exp\left[im\left(\phi + nZ\left(\alpha_0 + \frac{\pi}{Z} + \gamma\right)\right)\right] \exp\left(-\frac{\gamma^2}{4\delta^2}\right) d\gamma \\ &= \exp\{im(\phi + nZ\alpha_0 + n\pi)\} \exp\{-(mnZ\delta)^2\} \end{aligned} \quad (39)$$

where, in the interests of simplicity, the extension of the range of integration to $\pm\infty$ has not been taken too seriously.

It is clear that the effect of this component of the nearest-neighbour ensemble average operator $\langle \mathcal{R}(\alpha) \rangle_1$ has been to perform a generalized rotation upon the angular coordinate ϕ and at the same time to multiply the wave function by an exponential factor less than unity. So sharp is the variation of this factor that, for δ greater than about $\pi/2Z$, only terms with $m = 0, \pm 1$ and $n = 0, 1$ remain in ψ . This may be taken to apply to the sort of liquid we are considering, since Z is at least 3 and $\pi/6$ does not represent an unduly large distortion. It is, of course, possible to carry through further terms but this complicates the algebra and is not necessary for our present discussion.

Turning to non-nearest-neighbour atoms, we have assumed these to have no correlation in orientation with the central atom. This is in agreement with our treatment of nearest neighbours since, on this basis, the orientational uncertainty of next-nearest neighbours amounts to $\pm 2\delta$ which is greater than π/Z . Thus, from a treatment similar to (39), we find

$$\langle \exp(inZ\alpha) \rangle_2 \exp(im\phi) = \exp(im\phi) \delta_{n0}. \quad (40)$$

Substituting all these relations back into (27) and collecting up from it the terms in $J_m(\kappa\rho) \exp(im\phi(\rho))$, which are linearly independent of the other terms involved, and introducing the abbreviated notation

$$[J_m, R_{m'}] \equiv \left\{ J_m(\kappa\rho') \frac{d}{d\rho'} R_{m'}(\rho') - R_{m'}(\rho') \frac{d}{d\rho'} J_m(\kappa\rho') \right\}_{\rho' = r_s - \epsilon} \quad (41)$$

$$\Delta_Z \equiv \exp(-Z^2\delta^2) \quad (42)$$

$$\mathcal{B}_{mm'}^{\alpha,i} \equiv B_{mm'}^{(i)} \langle \mathcal{R}(\alpha) \rangle_i \quad (43)$$

we find

$$\sum_{m'} ([H_m^{(1)}, R_{m'}] \{\beta_{m'0} + \beta_{m'1} \exp(iZ\alpha)\} \delta_{mm'} + B_{mm'}^{(1)} [J_m, R_{m'}] \left[\beta_{m'0} + \beta_{m'1} \exp\left\{iZ\left(\alpha + \frac{\pi}{Z}\right)\right\} \Delta_Z \right] + B_{mm'}^{(2)} [J_m, R_{m'}] \beta_{m'0}) = 0. \quad (44)$$

This represents a set of independent equations for different values of m .

As remarked before, we can increase the number of independent equations by taking several different values of α . In the present case only two such equations are needed and, since two arbitrary values of α suffice, we choose $\alpha = 0, \pi/Z$. It is easily verified that the final result is independent of this particular choice.

If we define

$$\Lambda_m \equiv [H_m^{(1)}, R_m] / [J_m, R_m] \quad (45)$$

then the equations are

$$(\beta_{m'0} \pm \beta_{m'1}) \Lambda_m \delta_{mm'} + B_{mm'}^{(1)} (\beta_{m'0} \mp \beta_{m'1} \Delta_Z) + B_{mm'}^{(2)} \beta_{m'0} = 0 \quad (46)$$

and, after a little manipulation, the determinantal condition for their compatibility becomes

$$\det \begin{vmatrix} B_{mm'}^{(1)} + B_{mm'}^{(2)} + \Lambda_m \delta_{mm'} & 0 \\ 0 & -B_{mm'}^{(1)} \Delta_Z + \Lambda_m \delta_{mm'} \end{vmatrix} = 0. \quad (47)$$

We have used here a semi-condensed notation for the determinant in which, with each row or column labelled by a pair of indices n, m , we have written rows and columns explicitly for n and indicated the multiplicity of rows and columns for different m, m' values by subscripts. Thus (47) represents a $2M \times 2M$ determinant. The determinant is diagonal in n in the present case when only $n = 0, 1$ are allowed, but this is not true in general. If we restrict attention to angular momenta m, m' of 0 or ± 1 , then from (35) and (38) the determinant is also purely diagonal in m, m' in the present approximation.

5.2. Even co-ordination number

When Z is even the treatment is formally very similar to that above except that the average orientation of nearest neighbours is the same, rather than differing by π/Z . The expression corresponding to (44) thus differs from (44) by omission of π/Z from the exponent in the second term and, instead of (47), we finally arrive at

$$\det \begin{vmatrix} B_{mm'}^{(1)} + B_{mm'}^{(2)} + \Lambda_m \delta_{mm'} & 0 \\ 0 & B_{mm'}^{(1)} \Delta_Z + \Lambda_m \delta_{mm'} \end{vmatrix} = 0 \quad (48)$$

which differs formally from (47) just by the sign of one term. The explicit form of the various terms is, of course, different in the two cases.

6. Discussion

We have derived, in the form of (47) or (48), a determinantal equation in \mathbf{k} and κ involving the radial structure of the liquid through the terms $B_{mm}^{(i)}$, the angular correlations of nearest neighbours through Δ_Z , and the scattering behaviour of the individual atoms through the quantities Λ_m . Solution of this equation, as in the Kohn-Rostoker or Phariseau-Ziman treatments of crystals or liquids respectively, gives a relation between \mathbf{k} and κ . It is important now to see how our equations are related to both those for a crystal and those for a simple liquid and are, in a sense, intermediate between these two extremes.

First, let us consider the case in which angular correlations between nearest neighbours disappear. This occurs when the uncertainty δ in the bond orientations exceeds about π/Z so that $\Delta_Z \rightarrow 0$. It is clear in this case that it becomes impossible to define an orientation for the nearest-neighbour environment and the ensemble average gives spherical symmetry, as assumed in the Phariseau-Ziman treatment of simple liquids. Analytically we see that both (47) and (48) reduce essentially to

$$\det |B_{mm'}^{(1)} + B_{mm'}^{(2)} + \Lambda_m \delta_{mm'}| = 0 \quad (49)$$

which is the Phariseau-Ziman equation in two dimensions. The remaining rows and columns in the complete determinant are just $\Lambda_m \delta_{mm'}$, which, being diagonal and independent of \mathbf{k} , contribute nothing to the solution.

Let us consider now the case of a crystal with two like atoms per primitive cell, this implying an odd value of Z in the two-dimensional case. This problem has been treated in three dimensions by Segall (1957) and the two-dimensional equations will be similar in form. Using notation analogous to that in our discussion above, the crystalline secular equation becomes

$$\det |B_{mm'}^{(jj')} + \Lambda_m \delta_{mm'} \delta_{jj'}| = 0 \quad (50)$$

where the indices j and j' refer to the two sublattices on which the atoms lie and the elements of the determinant have the four indices m, m', j, j' . Writing rows and columns for the j, j' indices explicitly and performing a few obvious manipulations, (50) becomes

$$\det \begin{vmatrix} B_{mm'}^{(jj)} + \frac{1}{2}(B_{mm'}^{(jj')} + B_{mm'}^{(j'j)}) + \Lambda_m \delta_{mm'} & \frac{1}{2}(B_{mm'}^{(j'j)} - B_{mm'}^{(jj')}) \\ \frac{1}{2}(B_{mm'}^{(jj')} - B_{mm'}^{(j'j)}) & B_{mm'}^{(jj)} - \frac{1}{2}(B_{mm'}^{(jj')} + B_{mm'}^{(j'j)}) + \Lambda_m \delta_{mm'} \end{vmatrix} = 0 \quad (51)$$

where the writing has been simplified by noting that

$$B_{mm'}^{(jj)} = B_{mm'}^{(j'j')}.$$

From the explicit forms given by Segall it also follows that, at $\mathbf{k} = 0$ and for $m = m'$,

$$B_{mm}^{(jj')} = B_{mm}^{(j'j)}.$$

Thus, if only one value of m is considered, and at the zone centre only, (51) has a form similar to that of (47) and factors into two simple equations

$$B_{mm}^{(jj)} + B_{mm}^{(jj')} + \Lambda_m = 0 \quad (52)$$

and

$$B_{mm}^{(jj)} - B_{mm}^{(jj')} + \Lambda_m = 0. \quad (53)$$

The first of these equations, (52), is analogous to the upper equation derived from (47) when only a single m value is considered. It determines a band edge at $\mathbf{k} = 0$ for which the wave function has the same sign on the atoms of each sublattice and therefore constitutes bonding orbitals if m is even and antibonding orbitals if m is odd. This same character persists in a non-rigorous way over the whole band (Leman and Friedel 1962). Equation (53) corresponds to a band edge at $\mathbf{k} = 0$ for which the wave function has opposite sign on the two sublattices and so has antibonding character when m is even and bonding character when m is odd. In the liquid case in (47), since the two sublattices are indistinguishable past the nearest-neighbour shell, the term corresponding to $B_{mm}^{(jj)}$ vanishes and only the nearest-neighbour contribution $-B_{mm}^{(1)} \Delta_Z$ corresponding to the leading term of $-B_{mm}^{(jj')}$ remains.

It is thus clear that the energy bands of the liquid, derived from (47), have a one-to-one correspondence with those for the corresponding crystal with two atoms per unit cell and exhibit the same bonding or antibonding character in their wave functions. From the similarity of the coefficients involved in the liquid and crystalline cases we should expect that, near $\mathbf{k} = 0$, the energies determined in the two cases will also be very similar, provided the angular correlation is strong so that Δ_Z is not much less than unity.

An interesting and important phenomenon occurs as the angular correlation between nearest neighbours is relaxed. Let us consider the liquid analogue of (53), giving a band whose wave functions are alternating in sign at $\mathbf{k} = 0$. From (47) this is

$$-B_{mm}^{(1)} \Delta_Z + \Lambda_m \delta_{mm'} = 0 \quad (54)$$

which, from (43), (38) and (36), has the explicit form

$$N \int_0^\infty J_0(kx) H_0^{(1)}(\kappa x) g_1(x) dx = \Lambda_m / \Delta_Z. \quad (55)$$

Here Λ_m is a complex constant. To solve (55) we may take either one of k or κ to be real and fixed in value and then solve for the other, which will necessarily be complex in general,

though the imaginary part may be small. As the angular correlation of nearest neighbours is reduced, however, Δ_z tends to zero and the right side of (55) to infinity. From the behaviour of $J_0(z)$ and $H_0^{(1)}(z)$ for complex z (Jahnke and Emde 1945) this implies that the imaginary part of either k or κ must also tend to infinity. The band of allowed energy levels associated with this solution therefore disappears. On the other hand, this loss of angular correlation has, in this approximation, no effect upon the band derived from wave functions of the symmetrical-sign type and given by the analogue of (52).

The case of a liquid with even co-ordination number Z corresponds to a crystalline solid with just one atom per primitive cell. In this case both the solutions provided by (48) correspond to (\mathbf{k}, κ) relations for wave functions which, at $\mathbf{k} = 0$, are of the same sign on all the atoms of the system. Because the two equations derived from (48) are very similar, rather than differing in an important sign as in (47), they should lead to energy bands which overlap. This then provides only a small correction to the density of states derived from the Phariseau-Ziman equation, rather than giving rise to qualitatively new bands. Again the new states will disappear as the angular correlation is reduced.

This disappearance of whole bands may seem impossible from the viewpoint of the crystalline case, but it must be remembered that a liquid has no Brillouin zone structure in any strict sense, even if one can define a region in \mathbf{k} space which corresponds in volume to a Brillouin zone and contains two states per atom (counting spin). If this is the case, then, as the angular correlation is reduced, this region of \mathbf{k} space grows from that appropriate to two atoms per unit cell to that appropriate to one. In some sense therefore we may expect the states lost from the disappearing bands to be added as states of large \mathbf{k} to their partner band with the same m value.

It is, perhaps, appropriate to remark that, in the absence of a Brillouin zone structure, and particularly with complex values of \mathbf{k} or κ , the density of states in energy cannot be simply evaluated from the $\kappa(\mathbf{k})$ surfaces by assuming a uniform density of states in \mathbf{k} space. This is obvious from consideration of a single localized eigenstate, for example a wave function on an isolated atom, and noting that, because of its localization, the extent of the wave function in \mathbf{k} space is large. Some of these problems have been considered by Lloyd (1967) who has developed techniques for evaluating the density of states in certain cases.

7. Extension to three dimensions

The type of angular correlation dealt with here for an artificial two-dimensional case also exists in three dimensions and it is to be expected that a similar treatment can be applied, though the analysis is necessarily much more complex.

Each atom in the liquid has an environment which approximates a certain point group symmetry and which has an orientation defined by Euler angles (α, β, γ) . We seek a generalized rotation operator \mathcal{R} which will leave the wave function invariant under the operations of the point group (or possibly under a wider set of operations, because the rotational symmetry of the problem about the direction of \mathbf{k} as axis may make a modified configurational averaging desirable) and which will, at the same time, adequately describe the possible modifications of the wave function under rotation. The most appropriate expansion of \mathcal{R} will probably be similar to (16) except that functions of angular momentum operators must be used instead of simple exponentials to describe rotations in three dimensions (Messiah 1962). It is from the non-commutativity of these operators that the analytical complications spring.

Whilst it is hoped to present a proper treatment of the three-dimensional case at a later stage, it is now possible, with reasonable confidence, to conjecture as follows.

The three-dimensional case of interest is that in which the point group of nearest neighbours in the liquid does not contain the inversion as an element. Nearest-neighbour atoms are then connected by a rotation which is not a symmetry operation of the point group, in the same way as are the atoms of a crystal with more than one atom per primitive cell. In this case, provided the co-ordination number is small and the angular correlation high, the liquid will exhibit bands corresponding to wave functions with bonding or antibonding symmetry at $\mathbf{k} = 0$ in the same way as does the corresponding crystal, and the energies of these bands near $\mathbf{k} = 0$ will be similar to those of the crystal. As the angular correlations are reduced so the bands corresponding to wave functions which are of opposite sign on

neighbouring atoms disappear, the states in these bands being added to the symmetric bands at large wave number.

8. Application to germanium

The band structure of crystalline germanium is now well known (for a review see Callaway 1964). The valence band and lower parts of the conduction band arise from atomic s and p orbitals which, on a tight-binding approximation, are hybridized to tetrahedrally directed sp^3 orbitals.

At $\mathbf{k} = 0$ the bottom of the valence band has symmetry Γ_1 and is formed essentially from a symmetric (bonding) combination of atomic s orbitals. The top of the valence band, $\Gamma_{25'}$, is an alternating-sign (bonding) combination of p orbitals and, in this approximation, is triply degenerate. The conduction band minimum at $\mathbf{k} = 0$ is $\Gamma_{2'}$, an alternating-sign (antibonding) combination of s orbitals and Γ_{15} (a symmetric-sign antibonding combination of p orbitals) lies rather higher, though this branch actually forms the band edge at the zone-boundary point L. Spin-orbit coupling splits the degeneracy of $\Gamma_{25'}$ and Γ_{15} at $\mathbf{k} = 0$. This is shown in figure 2(a).

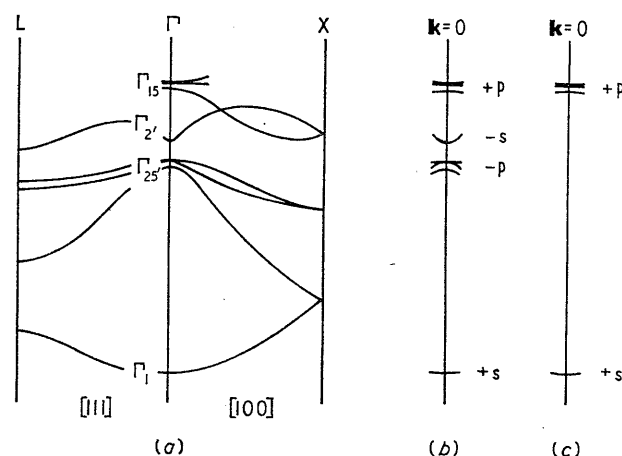


Figure 2. (a) Band structure of crystalline germanium. States at Γ , the zone centre, are labelled neglecting spin-orbit coupling. (b) Band structure suggested by the theory for amorphous germanium near $\mathbf{k} = 0$. + states are the same on each atomic site while - states differ in sign on nearest neighbours. (c) Band structure suggested by the theory for liquid germanium near $\mathbf{k} = 0$. The 'allowed region' in \mathbf{k} space is twice as large in (c) as in (b).

In amorphous germanium the tetrahedral co-ordination is thought to be maintained. The tetrahedral point group does not contain the inversion and $Z = 4$ is the smallest possible co-ordination number. We therefore expect, on the basis of our two-dimensional treatment, that amorphous germanium should have a band structure similar to that of crystalline germanium. The spin-orbit coupling, being also large in the isolated atom, should split the $\Gamma_{25'}$ and Γ_{15} states as before. This situation is shown schematically in figure 2(b).

Liquid germanium, if only because of its high temperature, will have much weaker angular correlation than amorphous germanium, though the co-ordination number is still only about 5. If we assume the angular correlation to have broken down so that $\Delta_Z \rightarrow 0$, then the bands represented in the crystal at $\mathbf{k} = 0$ by $\Gamma_{25'}$ and $\Gamma_{2'}$ will have disappeared and become absorbed in Γ_{15} and Γ_1 respectively. The two bands which have disappeared are those critically responsible for semiconductivity. The liquid now simply has an s band, which will be filled, followed at a higher energy by a p band which will be partly filled, as is shown schematically in figure 2(c). It is thus little surprise that liquid germanium behaves as a metal.

9. Conclusion

The most important conclusions to be drawn from this work are not those relating to amorphous germanium, which are somewhat speculative and are based upon a particular model for its possible structure, but rather those general assertions which can now be made about the relation between short-range order, and angular correlations in particular, and the band structure of a liquid or amorphous solid. These have only been explicitly demonstrated in two dimensions but there does not appear to be any reason why they cannot be extended in essentially the same form to the three-dimensional case.

The prime assertion is that the existence of a high degree of angular correlation between nearest-neighbour atomic positions is sufficient for the existence of band edges with wave functions of bonding and antibonding character at $\mathbf{k} = 0$, provided that the point group of the average nearest-neighbour environment does not contain the inversion as an element. This is true irrespective of the fact that it is impossible to define two independent sublattices in the liquid as can be done in the corresponding crystal. We are therefore led to the conclusion that many of the gross features of the band structure of a material are determined by its short-range order, irrespective of the existence of long-range order. This would indeed be expected on a 'chemical-bond' picture of the electronic structure, but has now been demonstrated using an approach which can include an adequate treatment of metallic structures.

At $\mathbf{k} = 0$ those band edges which correspond to wave functions of essentially opposite sign on nearest neighbours depend rather critically upon the degree of angular correlation between nearest neighbours. As this correlation is relaxed, the propagation vector acquires an increasingly large imaginary part, corresponding to increased scattering of the coherent wave, and the band gradually disappears. Those states which would have been assigned to it are transferred, as states of large \mathbf{k} , to a related band.

The generalized coherent-wave approximation developed here seems to offer a useful new approach to electronic structure calculations in disordered materials and also in such materials as finely polycrystalline solids.

Acknowledgments

This work was carried out during tenure of a Nuffield Fellowship at Bristol University. It is a pleasure to thank Professor J. M. Ziman for suggesting this investigation and for his interest and encouragement during its course. I have also profited greatly from many discussions of related matters with other members of the Theoretical Physics group.

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