

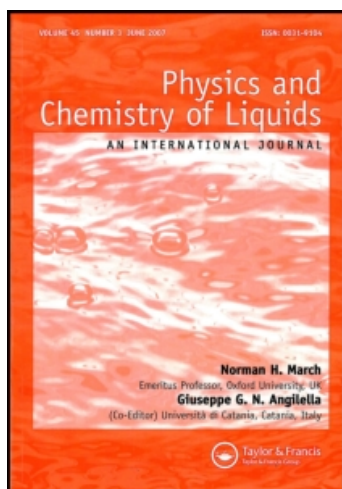
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The Energy Distribution of Electronic States in a Liquid Metal

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Abstract—A method is developed for calculating for a liquid metal the total number of electronic states below an energy E . The method remains valid when the electron-ion pseudopotential is energy dependent. It is based upon an idea of Lloyd (1967), which we have extended and developed into a form suitable for numerical calculation. Calculations for liquid bismuth reveal no sharp structure in the density of states. The bandwidth for five valence electrons per atom is 1.18 Ry, which corresponds to a bandwidth effective mass of 0.63 electron mass, compared with the first order perturbation estimate of 0.87.

1. Introduction

The number of calculations of the electronic structure of liquid metals is very small in comparison with the number of such calculations for solid metals. This fact reflects both the greater novelty and the greater difficulty of the problem for liquids. For example, it is in principle not possible to classify electron states by a wavevector \mathbf{k} or to obtain a unique energy versus \mathbf{k} relation.

Edwards (1962) showed how the density of electronic states per unit energy could be obtained from a perturbation expansion of the single particle Green function averaged over the ensemble of possible atomic arrangements appropriate to the liquid state. The first quantitative application of Edwards' formalism was by Ballentine (1966), who found the density of states of liquid Al and Zn to be nearly free-electron-like, but predicted that of liquid Bi to differ significantly from the free-electron parabola. Ballentine represented the electron-ion interaction by a local pseudopotential derived from

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the Fermi energy shell matrix elements of the Heine-Abarenkov model potential.

If the imaginary part of the Green function is very small one can, at least approximately, define a dispersion relation relating electron energy E to a wavevector k . By such a method Watabe and Tanaka (1964) predicted a very large peak near the Fermi energy in the density of states of liquid Zn. However, their result was shown to be entirely spurious (Ballentine, 1966), due in part to their use of a very crude approximation (an exponentially screened coulomb potential) to the electron-ion pseudopotential. Shaw and Smith (1969) have performed a similar calculation for Li, Cd, and In, using a non-local energy-dependent model potential. Their results resemble the densities of states of the corresponding solids but with all van Hove singularities smoothed out. Only for Li is their result much different from the free-electron curve. A similar calculation for nine metals has been reported by Srivastava and Sharma (1969), however, they give only the density of states at the Fermi level and not the entire curve. The limitations of this approach are the use of second order perturbation theory and the assumption of an $E(k)$ relation for a liquid. Both become suspect as the electronic structure becomes non-free-electron-like, which is of course the most interesting case. Although one can artificially define an $E(k)$ for a liquid such that it yields the correct density of states, that same $E(k)$ cannot be used for other applications such as the Boltzmann equation (Lloyd, 1968).

The work of Shaw and Smith (1969) indicates that retaining the non-local and energy-dependent nature of the model potential will tend to smooth out some of the structure predicted from a local pseudopotential. This is not surprising, for Ballentine (1966) found that the relative position of the zero of the pseudopotential (in momentum space) and the peak of the structure factor is an important parameter, and for a non-local pseudopotential the zero is effectively varying with energy or momentum. It requires only some additional numerical computation to include a non-local model potential in a calculation such as that of Ballentine (1966), but the energy dependence of the model potential causes difficulties in principle for the Green function method. It is the solution of these difficulties which is the subject of this paper.

The work of Ballentine (1966) and the present paper are not

strictly perturbation methods since infinite classes of terms are summed by means of integral equations. Nevertheless, they are weak binding approximations.

Cyrot-Lackmann (1966) has developed a tight binding approximation for the moments of density of states function. It is applicable only to strictly bound bands, since moments do not exist for free-electron-like bands. Lloyd (1967) has developed an interesting theory which uses the phase shifts of (assumed) non-overlapping ions rather than a pseudopotential. No realistic calculations have been done with his method, but he has shown by means of a simple model that his theory can describe the formation of a gap between a "free" and a "bound" band as the potential strength increases. Rousseau, Stoddard and March (1970) have developed a form of strong coupling theory based on the density matrix, rather than the Green function, and have applied their method to Be. They find the density of states to be qualitatively similar in the liquid and solid phases, and quite different from what it would be for a random distribution of atoms.

This brief review is believed to cover all quantitative calculations of the electronic density of states for liquid metals which have been published (excluding one dimensional models and disordered lattices).

2. The Problem of an Energy Dependent Potential

In order to see the difficulty introduced by the use of an energy dependent model potential, it is useful to review the Green function formalism (Edwards 1962; Ballentine 1966). The Green operator is defined as

$$G(E) = (E - H)^{-1} \quad (1)$$

$$= \sum_n \frac{|\psi_n\rangle\langle\psi_n|}{E - E_n}, \quad (2)$$

where H is the single electron hamiltonian, and $|\psi_n\rangle$ and E_n are its eigenvectors and eigenvalues. The spectral function,

$$\begin{aligned} \rho(\mathbf{k}, E) &= \lim_{\eta \rightarrow 0^+} (-1/\pi) \text{Im} \{ \langle \mathbf{k} | G(E + i\eta) | \mathbf{k} \rangle \} \\ &= \sum_n |\langle \mathbf{k} | \psi_n \rangle|^2 \delta(E - E_n), \end{aligned} \quad (3)$$

tells us the momentum distribution of electrons with energy E . The trace of the spectral function (considered to be the diagonal matrix

element of the spectral operator) gives us the density of states per unit energy per spin state,

$$\begin{aligned} \sum_{\mathbf{k}} \rho(\mathbf{k}, E) &= \sum_n \delta(E - E_n) \\ &= n(E). \end{aligned} \quad (4)$$

Suppose now that we take the hamiltonian to be $H = p^2/2m + W(E)$ ($= H(E)$, say), the electron-ion interaction being represented by the energy dependent model potential $W(E)$. Its eigenvectors and eigenvalues will be energy dependent,

$$H(E) | \phi_n(E) \rangle = \epsilon_n(E) | \phi_n(E) \rangle. \quad (5)$$

The true energy levels are obtained when the parameter E in the model potential is equal to the current eigenvalue, that is,

$$E_n = \epsilon_n(E_n). \quad (6)$$

Now, when we try to calculate the Green operator, as only we know how, from (1), we obtain results similar to (2)–(4) but with $\epsilon_n(E)$ instead of the true eigenvalue E_n . Thus, in place of (4), we obtain

$$\sum_n \delta(E - \epsilon_n(E)) = \sum_n \left\{ 1 - \frac{\partial \epsilon_n}{\partial E} \bigg|_{E = E_n} \right\}^{-1} \delta(E - E_n), \quad (7)$$

which is not equal to the density of states.

Lloyd (1967) showed that one could formally circumvent this difficulty by calculating the integrated density of states using the equation

$$N(E) = \frac{-1}{\pi} \text{Tr Im} [\ln \{H - (E + i\eta)\}]. \quad (8)$$

It is easy to show that [8] indeed evaluates the total number of eigenstates up to the energy E regardless of the energy dependence of the model potential. Thus, from (8), we have

$$\begin{aligned} N(E) &= \frac{-1}{2\pi i} \text{Tr} [\ln \{H - (E + i\eta)\} - \ln \{H - (E - i\eta)\}] \\ &= \frac{-1}{2\pi i} \sum_n [\ln \{\epsilon_n(E) - (E + i\eta)\} - \ln \{\epsilon_n(E) - (E - i\eta)\}] \\ &= \sum_n \theta \{E - \epsilon_n(E)\}, \end{aligned} \quad (9)$$

where the step function $\theta(x)$ is equal to unity for $x > 0$ and is zero for $x < 0$.

The last step follows from the fact that the value of the logarithm changes discontinuously from $-i\pi$ to $+i\pi$ as one crosses the branch cut on the negative real axis. Equation (9) says that $N(E)$ is equal to the number of eigenvalues $\epsilon_n(E)$ of $H(E)$ which are less than E . The true eigenvalues E_n are determined from Eq. (6). The number of these below energy E will also be given by $N(E)$ provided that $\partial\epsilon_n/\partial E$ is less than unity, that is as E increases $\epsilon_n(E)$ must not increase so rapidly that a level ϵ_n from just below E rises above E .

3. A Perturbation Expansion

The formalism for the integrated density of states presented in the last section is similar to that of Edwards, except that where the Green function occurs in Edwards' formalism, we now have the logarithm. It might appear from the similarity that we could employ Edwards' technique of expanding in a formal perturbation series, taking the ensemble average and resumming the terms. However, an examination of the diagrammatic expansion reveals that such a straightforward analogy with Edwards' method will not work.

Consider the operator

$$\ln(H - E) = \ln\{(H_0 - E)(1 - G_0W)\}, \quad (10)$$

where $H = H_0 + W$, and $G_0 = (E - H_0)^{-1}$ is the free electron Green operator. The energy dependence of G_0 and W is not explicitly indicated. Now $\ln(AB) \neq \ln(A) + \ln(B)$, in general, if the operators A and B do not commute. Nevertheless, one still has equality of the traces of the operators.

$$\begin{aligned} \text{Tr} \ln(AB) &= \ln(\det | AB |) \\ &= \ln(\det A) + \ln(\det B) \\ &= \text{Tr} \ln A + \text{Tr} \ln B. \dagger \end{aligned} \quad (11)$$

From (8), (10), and (11), we then obtain

$$N(E) = -\frac{1}{\pi} \text{Tr} \text{Im} \{\ln(H_0 - E) + \ln(1 - G_0W)\}. \quad (12)$$

The first term is just $N_0(E)$, the number of energy levels below E for the free electron hamiltonian H_0 .

† We are indebted to Dr. P. Lloyd for pointing out this relation.

To evaluate the second term it is natural to try a formal expansion,

$$-\ln(1 - G_0 W) = G_0 W + \frac{1}{2} G_0 W G_0 W + \frac{1}{3} G_0 W G_0 W G_0 W + \dots \tag{13}$$

The ensemble average, $\langle \langle \mathbf{k} | -\ln(1 - G_0 W) | \mathbf{k} \rangle \rangle_{\text{ave}}$, of the diagonal matrix element in the momentum representation can be represented by the diagrammatic series shown in Fig. 1. The notation here is the same as that of Ballentine (1966). A solid line represents a factor $(E - k^2)^{-1}$, an intersection of two solid lines with a dashed line represents a factor $\langle \mathbf{k} | w | \mathbf{k}' \rangle$, the matrix element of the screened model potential for a single ion, and a node connecting n dashed lines represents a factor \bar{C}_n , related to the n -particle correlation function.

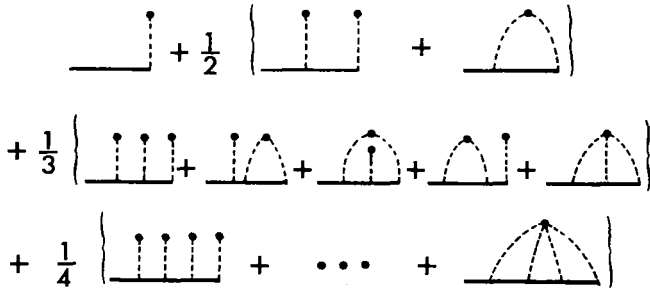


Figure 1. Diagrammatic representation of $-\langle \langle \mathbf{k} | \ln(1 - G_0 W) | \mathbf{k} \rangle \rangle_{\text{ave}}$.

If the n^{-1} factors were not present, we would be able to sum up “propagator renormalization” diagrams of all orders. Indeed, since these diagrams differ from ordinary Green function diagrams only by the lack of a G_0 line on their right hand ends, the sum of all diagrams omitting n^{-1} factors would be $(G - G_0) G_0^{-1}$.

The troublesome n^{-1} factors can be eliminated if we consider instead the expression $-\lambda(d/d\lambda) \ln(1 - G_0 \lambda W)$. This can be represented by the same diagrams as in Fig. 1 except that now the vertex corresponds to $\lambda \langle \mathbf{k} | w | \mathbf{k}' \rangle$ and the n^{-1} factors are absent. Examining the set of diagrams, we see that they are those for the ensemble average diagonal matrix element of $(G_\lambda - G_0) G_0^{-1}$, or equivalently of $G_\lambda \lambda W$. Here we have defined a Green operator

$$G_\lambda(E) = [E - H_0 - \lambda W(E)]^{-1}. \tag{14}$$

Its ensemble average diagonal matrix element can be written in the form

$$\langle \langle \mathbf{k} | G_\lambda(E) | \mathbf{k} \rangle \rangle_{\text{ave}} = [E - k^2 - \Sigma_\lambda(k, E)]^{-1}, \quad (15)$$

where the self-energy function $\Sigma_\lambda(k, E)$ is defined by this equation and is formally given by the sum of all irreducible diagrams (Edwards, 1958, 1962; Ballentine, 1966).

The result of this diagrammatic analysis is

$$\begin{aligned} \left\langle - \langle \mathbf{k} | \lambda \frac{d}{d\lambda} \ln(1 - G_0 \lambda W) | \mathbf{k} \rangle \right\rangle_{\text{ave}} \\ = \langle \langle \mathbf{k} | (G_\lambda - G_0) G_0^{-1} | \mathbf{k} \rangle \rangle_{\text{ave}} \\ = \Sigma_\lambda(k, E) [E - k^2 - \Sigma_\lambda(k, E)]^{-1}. \end{aligned} \quad (16)$$

The problem of evaluating (12) is thus reduced to the computation of the self-energy function Σ_λ of a Green operator containing λW as the potential energy, and familiar techniques and approximations (Ballentine, 1966) may be used.

The result (16) can also be derived algebraically without reference to diagrams, as is done in the appendix, but it is unlikely that we would have discovered it without diagrammatic analysis.

Writing

$$M(\lambda, E) = - \frac{1}{\pi} \left\langle \text{Im Tr} \left\{ \lambda \frac{d}{d\lambda} \ln(1 - G_0 \lambda W) \right\} \right\rangle_{\text{ave}}, \quad (17)$$

we have, from (16),

$$\begin{aligned} M(\lambda, E) &= \frac{1}{\pi} \frac{L^3}{(2\pi)^3} \int \text{Im} \left\{ \frac{\Sigma_\lambda(k, E)}{E - k^2 - \Sigma_\lambda(k, E)} \right\} d^3k \\ &= \frac{L^3}{2\pi^3} \int_0^\infty \text{Im} \left\{ \frac{\Sigma_\lambda(k, E)}{E - k^2 - \Sigma_\lambda(k, E)} \right\} k^2 dk, \end{aligned} \quad (18)$$

where L^3 is the normalization volume. In terms of $M(\lambda, E)$ equation (12) becomes

$$N(E) = N_0(E) + \int_0^1 \frac{M(\lambda, E)}{\lambda} d\lambda. \quad (19)$$

In (19) it is understood that $N(E)$ now represents the ensemble average number of states.

Although we have overcome the problem of an energy dependent model potential in calculating the number of states $N(E)$, we are now unable to determine any spectral information about the states.

Just as the diagonal matrix element of the Green operator (1) yields the spectral function $\rho(k, E)$, (3), whose trace is the density of states per unit energy (4), so the diagonal matrix element of $\ln(H - E)$ will yield the quantity

$$\int_{-\infty}^E \rho(\mathbf{k}, E') dE'.$$

But it was necessary for us to replace $\ln(H - E)$ by another operator with the same trace (using (11)) in order to do perturbation theory. Thus we have given up the possibility of obtaining information about the spectral function.

4. Application to Bismuth

To apply Eqs. (18) and (19) in a practical calculation we have to evaluate $\Sigma_\lambda(k, E)$ for different values of the parameter λ between 0 and 1. We evaluate $\Sigma_\lambda(k, E)$ by solving self-consistently the integral equation (see Ballentine 1966)

$$\Sigma_\lambda(k, E) = n\lambda u(\mathbf{k}, \mathbf{k}, E) + \frac{n\lambda^2}{(2\pi)^3} \int \frac{|u(\mathbf{k}, \mathbf{k}', E)|^2 a(|\mathbf{k}' - \mathbf{k}|) d^3k'}{E - k'^2 - \Sigma_\lambda(k', E)}$$

where

(20)

$$\begin{aligned} u(\mathbf{k}, \mathbf{k}', E) &= L^3 \langle \mathbf{k}' | w(E) | \mathbf{k} \rangle \\ &= \int \int \exp(-i\mathbf{k}' \cdot \mathbf{r}') \langle \mathbf{r}' | w(E) | \mathbf{r} \rangle \exp(i\mathbf{k} \cdot \mathbf{r}) d^3r d^3r' \end{aligned}$$

is the Fourier transform of the model potential, $n = N/L^3$ is the atomic density and $a(|\mathbf{k}' - \mathbf{k}|)$ is the structure factor measured by X-ray or neutron diffraction experiments. Here we have employed the units $\hbar = 1$, $2m = 1$ ($m =$ electron mass) and $a_0 \equiv \hbar^2/me^2 = 1$ (Bohr radius). It is to be noted that since a non-local model potential will be used, the first order term depends on k and E , and therefore cannot be set equal to zero by a shift of the origin. In terms of diagrams we are approximating the complete series of irreducible diagrams by the partial sum on Fig. 2, as in Ballentine (1966).

The structure factor of Bi (at 300 °C) has been taken from the neutron diffraction data of North, Enderby and Egelstaff (1968). We have used the non-local energy-dependent model potential of

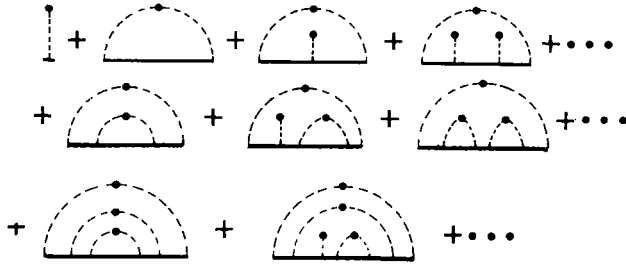


Figure 2. Diagrams summed by the integral Eq. (20).

Heine and Abarenkov (Heine and Abarenkov, 1964, Abarenkov and Heine, 1965, Animalu and Heine, 1965). Certain local potential contributions have been treated slightly differently from those papers, for reasons which are not particularly important here. Our Fermi energy shell form factor is shown in Fig. 3.

In order to solve Eq. (20) we first transform the integral into polar co-ordinates with the polar axis along the direction of \mathbf{k} so that

$$\Sigma_\lambda(k, E) = n\lambda u(k, k, E) + \frac{n\lambda^2}{2\pi^3} \int_0^\infty \frac{f(k, k', E)k^2}{E - k'^2 - \Sigma_\lambda(k', E)} dk. \quad (20')$$

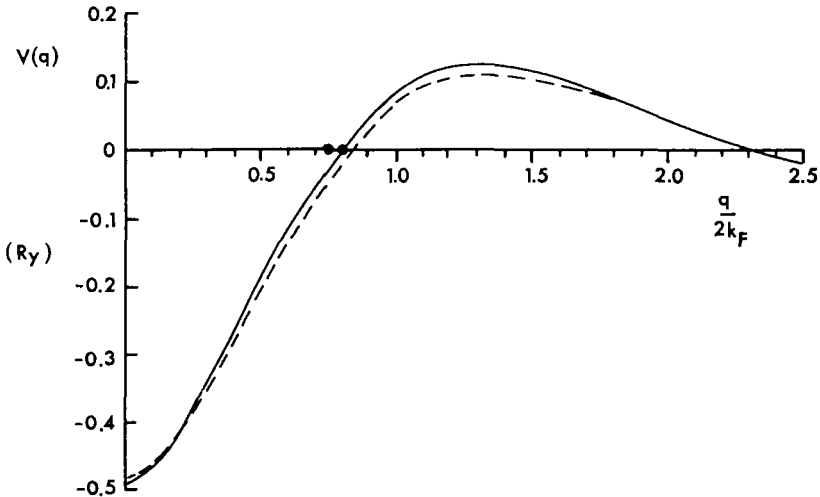


Figure 3. Model potential form factor for Bi. Solid curve: Fermi energy shell form factor used in this calculation. Dashed curve: Fermi energy shell form factor of Animalu and Heine (1965). Points: estimates of the node of form factor from liquid structure data (Cohen and Heine, 1970).

The angular integral yields

$$f(k, k', E) = \int_{-1}^1 |u(k, k', \mu, E)|^2 a(q) d\mu, \quad (21)$$

with μ being the cosine of the angle between \mathbf{k}' and \mathbf{k} and

$$q = (k^2 + k'^2 - 2kk'\mu)^{1/2}.$$

It can be tabulated for different values of k and k' , and need not be recalculated during the iterative solution of (20'). We use the assumed linear energy dependence of the model potential parameters $A_1(E)$, and hence of $u(E)$, to obtain the value of f at any energy E from its value at the Fermi energy. Equation (20') is then solved numerically by iteration for each particular value of E and λ (without making any approximation similar to the "complex energy approximation" of Ballentine (1966)). Further numerical integrations as indicated in (18) and (19) give $M(\lambda, E)$ and $N(E)$ respectively. The results are shown in Figures 4 and 5.

The numerical computation becomes inaccurate for very small values of λ . However, the limiting value of $M(\lambda, E)/\lambda$ as $\lambda \rightarrow 0$ can

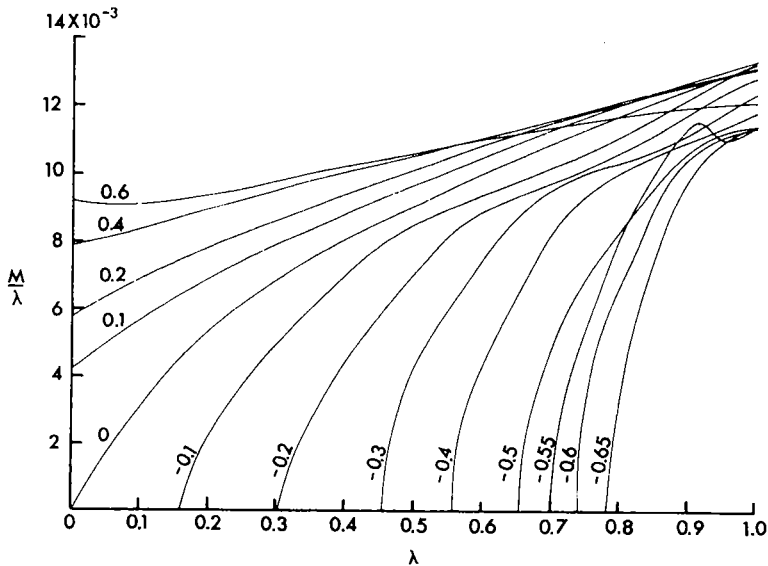


Figure 4. $M(\lambda, E)/\lambda$ (per unit volume) versus λ for several values of E . See (17) and (18) for the definition of this function.

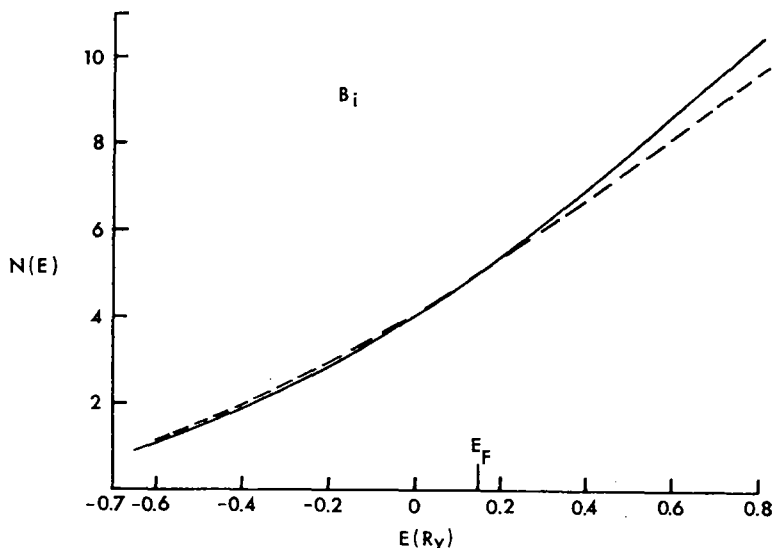


Figure 5. Number $N(E)$ of electronic states per atom below energy E , calculated for liquid bismuth at 300°C. Solid curve: calculated result. Dashed curve: best fitting free electron curve, corresponding to $m^*/m = 0.63$.

easily be obtained from (20') by treating λ as a perturbation parameter. The result for this limiting value is zero for negative E , and for positive E it is

$$-\frac{1}{4\pi^2} nu(\kappa, \kappa, E)\kappa, \quad \text{with } \kappa^2 = E.$$

Because the model potential parameters $A_i(E)$ are tabulated at the Fermi energy (Animalu, 1965), we must first estimate the position of E_F on our energy scale before we can begin the calculation. Using first order perturbation theory, we estimated it to be 0.246 on the scale of Fig. 5. However, it turns out that $N(E)$ equals 5 electrons per atom at $E = 0.146$. In principle, one could correct this inaccuracy of the first order initial approximation by readjusting E_F , the energy for which we use the tabulated parameters $A_i(E_F)$, until it became self-consistent with the energy value for which $N(E)$ equals 5 electrons per atom. Because of the very large amount of computer time needed for this calculation, we have not carried out this iteration to obtain a self-consistent Fermi energy. This means that the

model potential form factor which was actually used in the calculation at the point marked E_F on Fig. 5 was not the Fermi energy shell form factor shown in Fig. 3, but instead it was the form factor corresponding to an energy shell 0.1 Ry lower. The difference between these two form factors is very small (~ 0.005 Ry), and it is not likely to have a significant effect on the final results.

5. Discussion

The distribution of electron states (Fig. 5) calculated for bismuth has very little structure, and does not differ greatly from a $E^{3/2}$ free electron curve modified by an effective mass. (The zero of the energy scale has no absolute significance.) This can be seen more clearly in Fig. 6, where we have plotted $N^{2/3}$ versus E . The lower portion of the curve is well fitted by a straight line, which we have extrapolated from our lowest computed point ($E = -0.65$) to the bottom of the band. We obtain a bandwidth of 1.18 Ry, compared

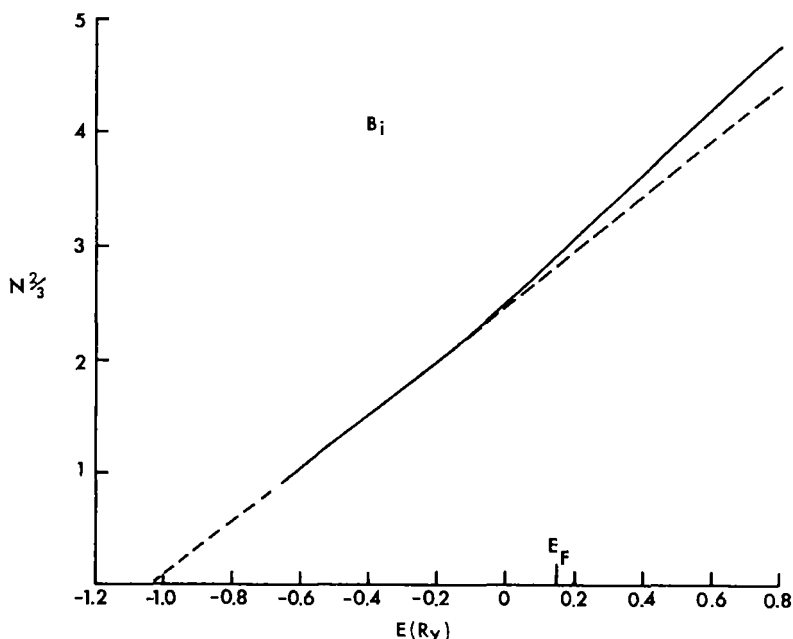


Figure 6. Similar to Fig. 5 but $N^{2/3}$ plotted. The free electron (dashed) curve is now a straight line.

with the free electron bandwidth of 0.74 Ry. The corresponding bandwidth effective mass is 0.63 m .

If one solves the first order perturbation equation,

$$E = k^2/2m + \langle \mathbf{k} | W(E) | \mathbf{k} \rangle,$$

and fits the solution to the form $E(k) = k^2/2m^* + E_0$, one obtains $m^*/m = 0.87$ (the same value was also found by Weaire (1967)). The smaller value of our bandwidth effective mass may be attributed to higher order contributions, and in particular to the energy dependence of the off diagonal matrix elements of the model potential. The fact that $E(k)$ does not really exist for a disordered system may also be relevant.

No remnant of the structure found in the density of states by Ballentine (1966) is apparent in our results. However, if his curve of the density of states per unit energy were integrated with respect to energy it would yield only a very small perturbation in $N(E)$. Furthermore, the non-local and energy dependent nature of our present model potential would tend to smooth out such structure, as was discussed in section 1.

The curves of $M(\lambda, E)/\lambda$ suggest some structure near $E = -0.55$, but it does not show up on the curve of $N(E)$.

The model potential which we have used was considered to be the best available at the time when the calculation was begun. Since then it has been demonstrated (Evans *et al.*, 1969, Evans, 1970) that the linear extrapolation of the model potential parameters $A_i(E)$ from the energies of excited ionic states to the energies of the conduction band in a metal (as was done by Animalu and Heine (1965)) may be inaccurate if the highest core level is a d-state. More reliable values of $A_i(E)$ and dA_i/dE at conduction band energies can be obtained by a nonlinear extrapolation using the quantum defect method (Ham, 1955). Evans showed that this nonlinear extrapolation has important consequences for mercury, in which the highest core levels are very close to the conduction band, but it is not known how important these effects would be for bismuth.

Appendix. Non-diagrammatic Derivation of Eq. (16)

If $A(\lambda)$ is an operator depending upon a parameter λ , then the

usual rule of calculus

$$d(\ln A)/d\lambda = A^{-1} dA/d\lambda$$

is valid, in general, only if the two operators A and $dA/d\lambda$ commute. For $A = (1 - G_0\lambda W)$, this condition is clearly satisfied. Hence

$$\begin{aligned} -\lambda \frac{d}{d\lambda} \ln(1 - G_0\lambda W) &= \lambda(1 - G_0\lambda W)^{-1} G_0 W \\ &= (G_0^{-1} - \lambda W)^{-1} \lambda W \\ &= (E - H_0 - \lambda W)^{-1} \lambda W \\ &= G_\lambda \lambda W. \end{aligned}$$

It is not convenient to calculate the ensemble average of this expression because both factors G_λ and W depend upon the arrangement of the ions. However, with a little manipulation one obtains

$$\begin{aligned} G_\lambda \lambda W &= G_\lambda (G_0^{-1} - G_\lambda^{-1}) \\ &= (G_\lambda - G_0) G_0^{-1}. \end{aligned}$$

This can be averaged directly because only G_λ depends upon the arrangement of the ions. Equation (16) now follows immediately upon taking the diagonal matrix element in momentum representation.

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