THE DENSITY OF STATES

This chapter shows how to define a density of electron states in terms of the electron Green function. Before going straight to this formulation, it is best to know what the density of states is, and in general how it can be calculated.

According to the Pauli principle not more than two electrons may occupy any orbital state, so that, at the absolute zero of temperature, two electrons will go into the ground state, two into each state of next higher energy, and so on, until all the electrons are allocated to states of lowest possible energy. In particular, it is possible, and useful, to define a density of states in energy $n(E)$ in the following way: the number of orbital states with energies lying between E and $E+dE$ is $n(E)$.

Here it is assumed that dE is very small but still large enough for the interval to contain very many states. It follows that the number of orbital states, $\nu(E)$ say, with energies less than E is

$$\nu(E) \; = \; \int_{0}^{E} n(E)\, dE \; ,$$

so that

$$n(E) \; = \; \frac{d\nu}{dE} \; .$$

As a simple example, let us consider the way in which the density of states of a free electron confined in a cubical box of side L can be obtained.

The Schrödinger equation for the free electron is

$$-\frac{\bar{h}^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z), \quad \text{-----}(2.1)$$

where $\psi(x,y,z)$ is the wave function which must fall to zero at the surface of the box, and E is the energy eigenvalues of the free electron.

By separating the partial differential equation and then imposing the boundary conditions on them, the wave function $\psi(x,y,z)$ and the energy eigenvalue E can be easily obtained, thus

$$\psi(x,y,z) = \sqrt{\frac{8}{L^3}}\ \sin\frac{n_x\pi x}{L}\ \sin\frac{n_y\pi y}{L}\ \sin\frac{n_z\pi z}{L}, \quad \text{----}(2.2)$$

$$E = \frac{\bar{h}^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right), \quad \text{-----}(2.3)$$

where n_x, n_y, n_z are integers.

It should be noted that changing the sign of n_x, n_y, or n_z does not change the energy, nor does it result in a different wave function. All the stationary states are therefore given by the positive integral values of n_x, n_y, n_z. Also, none of these may be zero, for this would make the wave function also zero, which is not permitted.

By looking at (2.3) in the n-space,

$$n_x^2 + n_y^2 + n_z^2 = \frac{2mL^2}{\bar{h}^2\pi^2}E,$$

it can be seen that it describes a sphere with radius $\left(\frac{2mL^2E}{\bar{h}^2\pi^2}\right)^{\frac{1}{2}}$.

We note, first of all, that each orbital state is represented by a triad of positive integral values of n_x,

n_y, n_z, and hence by a point in the positive octant of this n-space. Also, if we divide the octant up into unit cubic cells as shown in Fig.1, every point will represent a state lies at a corner of a cell, so that the unit volume contains just one representative point.

Thus, the number $\nu(E)$ of states with energies less than E is just the number of representative points lying within the positive octant of this sphere. Since there is one representative point per unit volume, therefore, this number is equal to the volume of the octant,

$$\nu(E) = \frac{1}{8} \frac{4\pi}{3} \left(\frac{2mL^2E}{\hbar^2 \pi^2} \right)^{3/2} = \frac{\Omega}{6\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{3}{2}} ,$$

where $\Omega = L^3$.

Differentiation with respect to E gives the density of states

$$n(E) = \frac{\Omega}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}} . \qquad \text{------} (2.4)$$

The graph representing density of states for a free electron system is shown in Fig. 2 .

From this example, it can be seen that the general way to find the density of states is to begin with the Schrödinger equation, solve for the wave functions and eigenenergies, and the result is the density of states. In applying the above method to the finding of the density of states of disordered systems, it is necessary to solve the Schrödinger equation (1.2) as many times as all possible arrangements of ions which is clearly impossible in practice. But by formulating a new procedure for the evaluation of the density of states using Green function formalism, the density of states of disordered systems can be found.
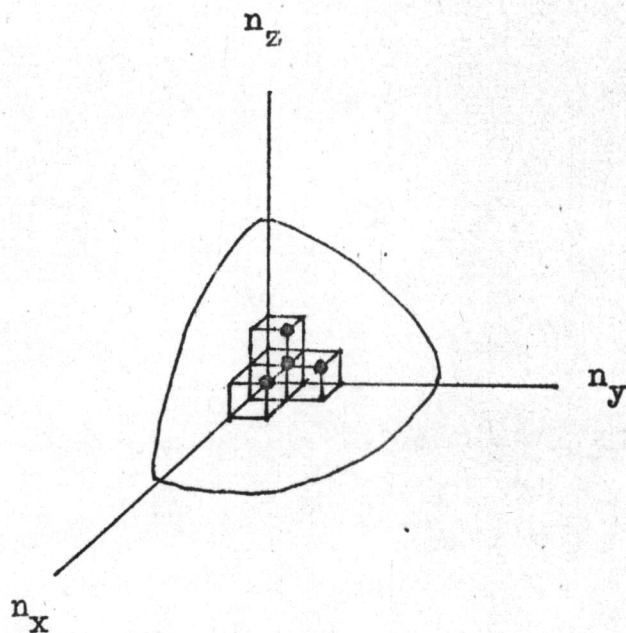
Fig. 1   The positive octant of n-space.
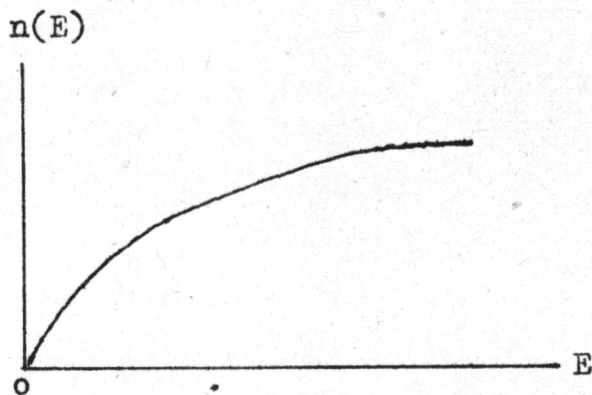The dots represent states.

Fig. 2   Density of states in energy for
a free-electron system.

For the Schrödinger equation (1.2) for an electron moving in the presence of fixed centers $\underline{R}_\alpha$ which give rise to the electron-center potentials $U(\underline{r}-\underline{R}_\alpha)$, we can define the one electron Green function $G(\underline{r},\underline{r}',t,t')$ of this equation as the solution of

$$\left[i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 - \sum_\alpha U(\underline{r}-\underline{R}_\alpha)\right] G(\underline{r},\underline{r}';t,t') = \delta(\underline{r}-\underline{r}')\,\delta(t-t').$$

$$------(2.5)$$

By applying the complex Fourier transform on the time variable and defining

$$G(\underline{r},\underline{r}';E)' = \int_{-\infty}^{\infty} G(\underline{r},\underline{r}';t,t')\exp\left[\frac{i}{\hbar}E(t-t')\right]dt$$

as the transform of $G(\underline{r},\underline{r}';t,t')$ on t, we obtain

$$\left[E + \frac{\hbar^2}{2m}\nabla^2 - \sum_\alpha U(\underline{r}-\underline{R}_\alpha)\right]G(\underline{r},\underline{r}';E) = \delta(\underline{r}-\underline{r}').$$

$$------(2.6)$$

Since the Hamiltonian H of the system is equal to $-\frac{\hbar^2}{2m}\nabla^2 + \sum_\alpha U(\underline{r}-\underline{R}_\alpha)$, and the delta function $\delta(\underline{r}-\underline{r}')$ can be written as the complete set of the wave fuctions,

$$\delta(\underline{r}-\underline{r}') = \sum_n \Psi_n(\underline{r})\,\Psi_n^*(\underline{r}').$$

Eq.(2.6) becomes

$$(E-H)\,G(\underline{r},\underline{r}';E) = \sum_n \Psi_n(\underline{r})\,\Psi_n^*(\underline{r}').$$

Therefore
$$G(\underline{r},\underline{r}';E) = (E-H)^{-1}\sum_n \Psi_n(\underline{r})\,\Psi_n^*(\underline{r}')$$

$$= (E-E_n)^{-1}\sum_n \Psi_n(\underline{r})\,\Psi_n^*(\underline{r}').$$

$$------(2.7)$$

A small imaginary term $\pm i\epsilon$ has to be added to the denominator of Eq.(2.7) in order that the pole at $E-E_n$ can be taken.

Therefore, there are two basic solutions of Eq. (2.6)

$$G_{\pm}(\underline{x}, \underline{x}'; E) = (E - E_n \pm i\epsilon)^{-1} \sum_n \Psi_n(\underline{x}) \Psi_n^*(\underline{x}'),$$

where G_+ corresponds to the outgoing wave and G_- to the incoming wave. Now since the functions Ψ_n are normalized

$$\int G_{\pm}(\underline{x}, \underline{x}; E)\, d\underline{x} = \sum_n (E - E_n \pm i\epsilon)^{-1},$$

and since

$$(E - E_n - i\epsilon)^{-1} - (E - E_n + i\epsilon)^{-1} = 2i\, \frac{\epsilon}{(E - E_n)^2 + \epsilon^2}$$

$$= 2\pi i\, \delta(E - E_n),$$

consequently

$$\int \left[G_+(\underline{x}, \underline{x}; E) - G_-(\underline{x}, \underline{x}; E) \right] d\underline{x} = -2\pi i \sum_n \delta(E - E_n).$$

$$\text{-----(2.8)}$$

From the definition of the Dirac delta function, $\delta(E-E_n)$ will always be zero except at the points where E_n equals E; hence $\sum_n \delta(E-E_n)$ in Eq.(2.8) is to be interpreted as the summation which indicates how many states of the electron have energy E, which by definition is the density of states. Thus, Eq. (2.8) becomes

$$\int \left[G_+(\underline{x}, \underline{x}; E) - G_-(\underline{x}, \underline{x}; E) \right] d\underline{x} = -2\pi i\, n(E),$$

$$\text{-------(2.9)}$$

where $n(E)$ is the density of states.

For disordered systems in which the distribution of ions has several configurations, the average density of states is obtained by averaging $n(E)$ over the configurations

of ions in the probability with which the various configurations occur. Denoting this averaging process by bracket $\langle \cdots \rangle$, we therefore have

$$\langle n(E) \rangle = \frac{i}{2\pi} \int \left[\langle G_+ \rangle - \langle G_- \rangle \right] d\underline{r} \; . \qquad \text{-------- (2.10)}$$

The averages of G_+ and G_- will be functions of $\underline{r}-\underline{r}'$ alone, as the averaged system must be spatially homogeneous.

Let $\rho\left(\underline{r}-\underline{r}'; t-t'\right) = \frac{i}{2\pi}\left[\langle G_+ \rangle - \langle G_- \rangle \right]$;

then Eq. (2.10) can be written in terms of $\rho(\underline{k},E)$, the Fourier transform of $\rho(\underline{r}-\underline{r}',t-t')$, as

$$\langle n(E) \rangle = \frac{\Omega}{(2\pi)^3} \int \rho\left(\underline{k},E\right) d^3k \; , \qquad \text{--------- (2.11)}$$

where Ω is the total volume, and $\rho(\underline{k},E)$ may be regarded as the probability of finding an electron with energy E and momentum $\underline{k}$.

In order to follow the method of evaluating the density of states of the electron with the use of this new expression (2.11), the evaluation for the density of states of the free electron system will be first considered.

Let $G_0(\underline{r},\underline{r}';t,t')$ be the free electron Green function satisfying the equation

$$\left[i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 \pm i\epsilon \right] G_{0_\pm}\left(\underline{r},\underline{r}'; t,t'\right) = \delta(\underline{r}-\underline{r}')\delta(t-t') \; .$$

By taking the Fourier transform with respect to t and $\underline{r}$, and defining

$$G_0\left(\underline{k},E\right) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} G_0\left(\underline{r},\underline{r}'; t,t'\right) \exp\left[-i\underline{k}\cdot(\underline{r}-\underline{r}')+\frac{i}{\hbar}E(t-t')\right] d\underline{r}\,dt,$$

we then obtain

$$\left[E - \frac{\hbar^2 k^2}{2m} \pm i\epsilon \right] G_{0\pm}(\underline{k}, E) = 1 \quad,$$

$$G_{0\pm}(\underline{k}, E) = \left[E - \frac{\hbar^2 k^2}{2m} \pm i\epsilon \right]^{-1}.$$

In the case of a free electron the distribution of ions is not concerned, so the free electron Green function and the density of states are not involved in the averaging process, therefore

$$\rho_0(\underline{k}, E) = \frac{i}{2\pi} \left[G_{0+}(\underline{k}, E) - G_{0-}(\underline{k}, E) \right]$$

$$= \frac{i}{2\pi} \left[2i \frac{\epsilon}{\left\{ \left(E - \frac{\hbar^2 k^2}{2m} \right)^2 + \epsilon^2 \right\}} \right]$$

$$= \delta \left(E - \frac{\hbar^2 k^2}{2m} \right) \quad,$$

and

$$n_0(E) = \frac{\Omega}{(2\pi)^3} \int \delta \left(E - \frac{\hbar^2 k^2}{2m} \right) d^3k$$

$$= \frac{\Omega}{(2\pi)^3} \int \delta \left(E - \frac{\hbar^2 k^2}{2m} \right) 4\pi k^2 dk . \quad \text{------ (2.12)}$$

By introducing a new variable $y = \frac{\hbar^2 k^2}{2m}$, Eq.(2.12) can be written as

$$n_0(E) = \frac{\Omega}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int \delta(E - y) \, y^{\frac{1}{2}} \, dy$$

$$n_0(E) = \frac{\Omega}{4\pi^2}\left[\frac{2m}{\hbar^2}\right]^{\frac{3}{2}} E^{\frac{1}{2}} \quad ,$$

which is exactly the same as was obtained previously in Eq. (2.4).

In the case of free electrons where the distribution of ions is not concerned, and also in the case of perfect crystals which have only one configuration of ions, the expression (2.11) for the evaluation of the density of states may not have much advantage over the general method. But the expression will be very useful in evaluating for the density of states of disordered systems, where the evaluations have to be taken as many times as the number of possible configurations of ions which may occur.

After seeing how the averaged density of states can be expressed in terms of the electron Green function and how the expression can be used, the next step is to try to find the averaged Green function of disordered systems. This chapter develops a method of finding the averaged Green function by performing an expansion in the form of a perturbation expansion of the free electron Green function.

Since from Eq. (2.6), we have

$$(E-H)\, G(\underline{x},\underline{x}';E) = \delta(\underline{x}-\underline{x}') \quad ,$$

therefore
$$G(\underline{x},\underline{x}';E) = (E-H)^{-1}\delta(\underline{x}-\underline{x}')$$

$$= \left[E-H_0-\sum_\alpha U(\underline{x}(\tau)-\underline{R}_\alpha)\right]^{-1}\sum_n \psi_n(\underline{x})\psi_n^*(\underline{x}')$$

$$\cdots\cdots (2.13)$$

where H_0 is the free electron Hamiltonian. Eq. (2.13) is the initial equation in writing G as a perturbation

expansion of the free electron Green function. Edwards was the first to perform this expansion. His first paper[8] was concerned with using the Green function in the perturbation expansion of the free electron Green function for the evaluation of the closed formal expression for the electrical conductivity of metals without going through the intermediate form of deriving a transport equation. His second paper[6] used this expression for evaluating the averaged Green function of disordered systems. In order to average G without difficulty Edwards considered its expansion in terms of the deviation of the potential $\sum_\alpha U(\underline{r}-\underline{R}_\alpha)$ from its mean. Hence Eq. (2.13) can be written as

$$G\left(\underline{r},\underline{r}';E\right) = \left[E - H_0 - \langle V\rangle + \langle V\rangle - V\right]^{-1},$$

where

$$V = \sum_\alpha U\left(\underline{r} - \underline{R}_\alpha\right).$$

Therefore

$$G\left(\underline{r},\underline{r}';E\right) = \left[E - H_0 - \langle V\rangle\right]^{-1}\left[1 - \frac{V - \langle V\rangle}{E - H_0 - \langle V\rangle}\right]^{-1}$$

$$= G_0\left[1 - \left\{G_0\left(V - \langle V\rangle\right)\right\}\right]^{-1}, \quad \text{------ (2.14)}$$

where G_0 satisfies the equation

$$\left[i\bar{h}\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 - \langle V\rangle\right]G\left(\underline{r},\underline{r}';t,t'\right) = \delta\left(\underline{r}-\underline{r}'\right)\delta\left(t-t'\right).$$

Eq. (2.14) can be expanded as a geometric series:

$$G\left(\underline{r},\underline{r}';E\right) = G_0\left[1 + \left\{G_0\left(V - \langle V\rangle\right)\right\} + \left\{G_0\left(V - \langle V\rangle\right)\right\}^2 + \cdots\right].$$

$$G(x, x'; E) = G_0 + G_0 (V - \langle V \rangle) G_0 + G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0$$

$$+ G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 + \cdots \cdots \quad .$$

Averaging this series over all the possible configurations of ions, we obtain

$$\langle G \rangle = G_0 + G_0 \langle (V - \langle V \rangle) \rangle G_0 + G_0 \langle (V - \langle V \rangle) G_0 (V - \langle V \rangle) \rangle G_0$$

$$+ G_0 \langle (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) \rangle G_0 + \cdots \cdots$$

$$\cdots \cdots (2.15)$$

Since $\langle V - \langle V \rangle \rangle = \langle V \rangle - \langle V \rangle = 0$

and since Edwards[8] has shown that when V is weak all the odd averages in the series (2.15) (except $\langle V \rangle$) are small compared with the even averages which precede them, therefore Eq. (2.15) becomes

$$\langle G \rangle = G_0 + G_0 \langle (V - \langle V \rangle) G_0 (V - \langle V \rangle) \rangle G_0$$

$$+ G_0 \langle (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) \rangle G_0 + \cdots \cdots (2.16)$$

Averaging, we obtain

$$\langle (V - \langle V \rangle) G_0 (V - \langle V \rangle) \rangle = \langle V G_0 V \rangle - \langle V \rangle G_0 \langle V \rangle \quad ,$$

$$\langle (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) G_0 (V - \langle V \rangle) \rangle = \langle V G_0 V G_0 V G_0 V \rangle - \langle V G_0 V \rangle G_0 \langle V G_0 \cdots$$

$$\cdots \cdots \cdots \cdots \cdots \cdots \quad .$$

Thus each average in the series (2.16) contains terms like $\langle V G_0 V \rangle$, $\langle V G_0 V G_0 V \rangle$, $\cdots \cdots$.

We consider the average $\langle VV \rangle$, and for simplicity will consider only the one-dimensional case.

$$\langle VV \rangle = \sum_{\alpha,\beta} \langle U(x_1 - R_\alpha) U(x_2 - R_\beta) \rangle$$

$$= \sum_{\alpha,\beta} \langle \iint u(k) \exp\left\{ ik(x_1 - R_\alpha) \right\} u(j) \exp\left\{ ij(x_2 - R_\beta) \right\} dk\, dj \rangle ,$$

where $u(k)$ is the Fourier transform of $U(x)$.

Since the system is assumed homogeneous which implies that the last expression must depend on $R_\alpha - R_\beta$ or that $j = -k$, therefore

$$\langle VV \rangle = \sum_{\alpha,\beta} \langle \int u(k) u(-k) \exp\left\{ ik(x_1 - x_2) \right\} \exp\left\{ ik(R_\alpha - R_\beta) \right\} dk \rangle$$

$$= \int u(k) u^*(k) \exp\left\{ ik(x_1 - x_2) \right\} a_2(k)\, dk ,$$

where

$$a_2(k) = \sum_{\alpha,\beta} \langle \exp\left\{ ik(R_\alpha - R_\beta) \right\} \rangle .$$

The function $a_2(k)$ is the two-body correlation in k-space, i.e. the Fourier transform of the probability that given one atom at x_1 another will be found at x_2.

Thus the problem in obtaining $\langle VV \rangle$ is that of finding $u(k)$ and $a_2(k)$, and we can similarly show that the problems in obtaining $\langle VVVV \rangle$, $\langle VVVVVV \rangle$, ... are also those of finding $u(k)$ and $a_4(k)$, $a_6(k)$, ... $a_{2n}(k)$, the 2n − body correlation function. Consequently, the problem of finding $\langle G \rangle$ in Eq. (2.16), and hence the density of states from Eq.(2.10) is also reduced to that of finding $u(k)$, $a_2(k)$ $a_4(k)$, ..., $a_{2n}(k)$. $u(k)$ and $a_2(k)$ can be theoretically determined after a model has been adopted. $a_2(k)$ can also be determined from the X-ray or neutron scattering

data. Since a_4 (k), a_6 (k) ...., a_{2n} (k) are not yet known, it is indeed fortunate that Edwards[9] is able to show that under certain circumstances concerning the relative magnitudes of the electron mean free path L and the range of order R, a_{2n} (k) can be factorized into products of a_2(k).

As an exercise, it is worth knowing how u(k) and a_2(k) can be theoretically determined by using the simplest model.

Let us take the one-dimensional disordered potential $\sum_\alpha U(r-R_\alpha)$ as a delta function potential, i.e.

$$\sum_\alpha U\left(x - R_\alpha\right) = \sum_\alpha \delta\left(x - R_\alpha\right).$$

By taking the Fourier transform of both sides, we obtain

$$\frac{1}{(2\pi)^3} \sum_\alpha \int u(k)\, exp\left\{ik(x-R_\alpha)\right\} d^3k = \frac{1}{(2\pi)^3} \sum_\alpha \int exp\left\{ik(x-R_\alpha)\right\}$$

Therefore the Fourier transform u(k) of the disordered delta function potential is a constant.

If we now take the one-dimensional disordered systems as completely disordered, the probability distribution will be given by

$$P\left(R_1 ----- R_N\right) = \prod_{\alpha=1}^{N} \frac{dR_\alpha}{\int \cdot dR_\alpha} .$$

Since

$$a_2(k) = \sum_{\alpha,\beta} \left\langle exp\left\{ik(R_\alpha-R_\beta)\right\}\right\rangle$$

$$= \sum_{\alpha \neq \beta} \left\langle exp\left\{ik(R_\alpha-R_\beta)\right\}\right\rangle + \sum_{\alpha=\beta} \left\langle exp\left\{ik(R_\alpha-R_\beta)\right\}\right\rangle$$

$$a_2(k) = \sum_{\alpha \neq \beta} \iint \exp\{ik(R_\alpha - R_\beta)\} \frac{dR_\alpha}{\int dR_\alpha} \frac{dR_\beta}{\int dR_\beta}$$

$$+ \sum_{\alpha = \beta} \iint \exp\{ik(R_\alpha - R_\beta)\} \frac{dR_\alpha}{\int dR_\alpha} \frac{dR_\beta}{\int dR_\beta}$$

$$= \frac{1}{L^2} \sum_{\alpha \neq \beta} \delta(k)\delta^*(k) + \frac{NL^2}{L^2} ,$$

therefore when $k \neq 0$ only the terms with $\alpha = \beta$ survive, i.e. $a_2(k) = N$ and when $k = 0$

$$a_2(k) = \frac{1}{L^2} \sum_{\alpha, \beta} \iint \exp\{ik(R_\alpha - R_\beta)\} \, dR_\alpha \, dR_\beta$$

$$= \frac{1}{L^2} \sum_{\alpha, \beta} \iint \exp\{0\} \, dR_\alpha \, dR_\beta = \frac{1}{L^2} N^2 L^2 = N^2 .$$

Edwards[6] was the first to evaluate $\langle G \rangle$ and hence the density of states of disordered systems, by the method which has just been discussed. He used the simplest model of a one-dimensional completely disordered system with a delta function potential. An extension to the case of three dimensions using the same model has also been made by Edwards[9]. The work of Edwards[6-9] has dealt only with the case of free bands. Beeby and Edwards[10] extend the calculations from free bands to bound bands by replacing the scattering potential by a t-matrix. Ballentine[12] has calculated the density of states from these formulae for certain liquid metals—alumi nium, zinc and bismuth—by taking the two-body correlation (the structure factor)$a_2(k)$ of aluminium and zinc from the X-ray scattering data of

Gammertsfelder[17] , that of bismuth from the neutron scattering data of Sharrah and Smith[18] and the screened ion potential u(k) from Heine and Abarenkov[19] .

Lukes[11] has used another method to obtain $\langle G \rangle$ from the series (2.16). In this paper the averages $\langle V \rangle$, $\langle VV \rangle$, $\langle VVV \rangle$,...in Eq. (2.16) can be obtained by assuming a multivariate gaussian distribution.

The density of states obtained from this method (i.e. evaluating $\langle G \rangle$ from the perturbation expansion of the free electron Green function and substituting into the expression (2.10) for the density of states) has nearly the same value as the experimental result as is shown in Fig. 3, but the exponential tail which is the important characteristic of disordered systems can not be obtained. So we must find another method to calculate the averaged Green function. Edwards and Gulyeav[13] have pointed out that, by using Feynman's path integral formalism, it is possible to express the averaged time-dependent Green function or the Feynman propagator of disordered systems in a closed form.

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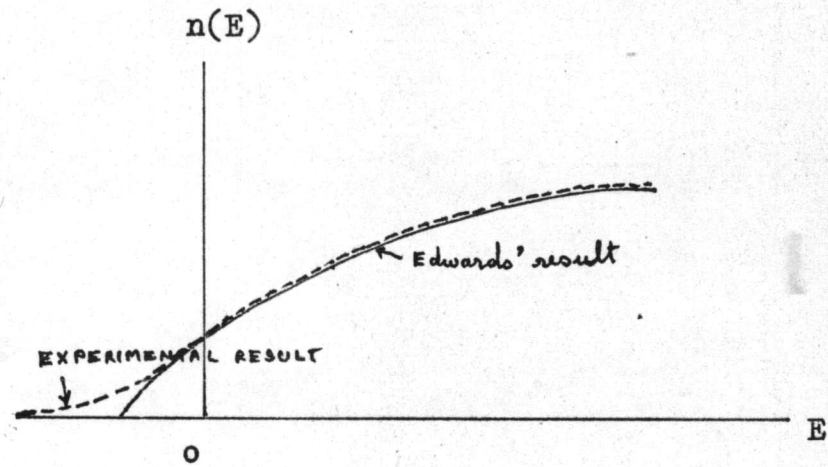
Fig. 3.   Density of states in energy for
disordered systems.