

Electrons in Disordered Systems

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I. Introduction

The subject of this paper is the behavior of electrons in systems for which the potential is not completely determined as a function of position, but is instead given by some probability distribution. The electrons will be assumed to be independent, so that the problem reduces to that of one electron. The available states are then filled with due regard to the Pauli principle. This formalism, developed by S. F. Edwards, applies equally well to independent quasi particles moving in an appropriate potential.

Consider a set of identical ions fixed at positions \mathbf{R}_i , $i = 1, 2, \dots, N$. If the potential around each ion is $v(\mathbf{r})$, the Schrodinger equation is

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_a v(\mathbf{r} - \mathbf{R}_a) - E_n \right] \psi_n(\mathbf{r}) = 0$$

and the propagator for the electron in this potential is

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \sum_a v(\mathbf{r} - \mathbf{R}_a) - E - i\varepsilon \right] G(\mathbf{r}, \mathbf{r}'; E) = -\delta(\mathbf{r} - \mathbf{r}')$$

and is given in terms of ψ_n by

$$G(\mathbf{r}, \mathbf{r}'; E) = \sum_n \frac{\psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')}{E - E_n + i\varepsilon}. \quad (1)$$

Now consider a system of such sets in which the particular set $\mathbf{R}_1, \dots, \mathbf{R}_N$ occurs with a probability distribution $P(\mathbf{R}_1, \dots, \mathbf{R}_N)$. The average of

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any function over this system will be denoted by Dirac brackets which thus correspond to the integration of the function with P over all $\mathbf{R}_1, \dots, \mathbf{R}_N$ space. Such a system may be formed by subdividing the given substance into a large number of smaller pieces or by taking the whole of the substance and considering its instantaneous distribution at different times. (There is no time dependence in the theory, which is therefore entirely within the adiabatic approximation.)

Take the Fourier transformation of (1), average it over the system, and take its imaginary part:

$$\langle \text{Im } G(\mathbf{k}, \mathbf{k}; E) \rangle = -\pi \left\langle \sum_n \psi_n(\mathbf{k}) \psi_n^*(\mathbf{k}) \delta(E - E_n) \right\rangle$$

(the two transformed variables have been put equal). The right-hand side is then the probability that in this system a state with energy $E = E_n$ has "momentum" \mathbf{k} . In other words the density of states with a given energy and momentum is a probability distribution

$$\varrho(\mathbf{k}, E) = -\text{Im } \pi^{-1} \langle G(\mathbf{k}, \mathbf{k}; E) \rangle$$

and the density of levels is now

$$n(E) = \int \varrho(\mathbf{k}, E) d\mathbf{k}$$

In an ordered system the brackets do not arise and if the spectrum is continuous one has $\varrho(\mathbf{k}, E) \propto \delta[E - E(\mathbf{k})]$, i.e., E and \mathbf{k} are directly related.

Our program will be to work out the propagator $G(\mathbf{k}, \mathbf{k}; E)$ and from it to evaluate the density of states. Transport properties such as conductivity, in general require averages over pairs of propagators and so are much harder to work out.

The technique to be used is that of formally expanding the propagator around the unperturbed propagator G_0 which satisfies

$$\left(-\frac{\hbar^2}{2m} \nabla^2 - E - i\varepsilon \right) G_0(\mathbf{r} - \mathbf{r}'; E) = -\delta(\mathbf{r} - \mathbf{r}').$$

In Fourier transform $G_0(\mathbf{k}; E) = (E - k^2 + i\varepsilon)^{-1}$. The expansion may then be averaged term by term and the series re-summed in an appropriate manner.

Thus

$$\langle G \rangle = G_0 + G_0 \langle \sum_a v_a \rangle G_0 + G_0 \langle \sum_a v_a G_0 \sum_\beta v_\beta \rangle G_0 + \dots \quad (2)$$

Consider first the case of weak potentials.

II. Weak Potentials

If the potential is weak then it is convenient to choose the zero of energy to be such that $\langle \sum_a v_a \rangle = 0$ (in the case of a homogeneous system), after which all terms involving odd powers of the potential will in general be small compared to the term following which has one extra power of v . If one now writes

$$\langle \sum_a v_a G_0 \sum_\beta v_\beta \rangle = \Sigma_2$$

and

$$\langle \sum_a v_a G_0 \sum_\beta v_\beta G_0 \sum_\gamma v_\gamma G_0 \sum_\delta v_\delta \rangle = \Sigma_2 G_0 \Sigma_2 + \Sigma_4$$

and so on, then a formally exact summation of Eq. (2) is given by

$$\langle G \rangle = (G_0^{-1} - \Sigma_2 - \Sigma_4 - \dots)^{-1}.$$

If Σ_4 is small compared with Σ_2 and is, in particular, well behaved near the zeros of $G_0^{-1} - \Sigma_2$, then this formal summation may be a good approximation to the correct answer. This approximation depends mainly on the degree of order in the system; it is very good for a random system or for a perfect lattice. The remaining step is to work out Σ_2 and the two extreme cases may be used to illustrate this process.

A. COMPLETE DISORDER

In Fourier transform

$$\begin{aligned} \Sigma_2 &= \langle \sum_{a\beta} v(\mathbf{x} - \mathbf{R}_a) G_0(\mathbf{x} - \mathbf{y}) v(\mathbf{y} - \mathbf{R}_\beta) \rangle \\ &= \langle \sum_{a\beta} \left(\frac{1}{2\pi} \right)^6 v(\mathbf{k}) v(\mathbf{j}) \exp(i\mathbf{k} \cdot \mathbf{R}_a + i\mathbf{j} \cdot \mathbf{R}_\beta) \rangle \\ &\quad \int \exp(-i\mathbf{k} \cdot \mathbf{x}) \exp(-i\mathbf{j} \cdot \mathbf{y}) G_0(\mathbf{x} - \mathbf{y}) dx dy \end{aligned}$$

so that the averaging is concentrated into

$$\langle \sum_{\alpha\beta} \exp(i\mathbf{k} \cdot \mathbf{R}_\alpha + i\mathbf{j} \cdot \mathbf{R}_\beta) \rangle \delta(\mathbf{k} + \mathbf{j}) .$$

If the \mathbf{R} 's are completely random only the $\alpha = \beta$ terms in the sum survive and then

$$\delta(\mathbf{k} + \mathbf{j}) \langle \sum_{\alpha\beta} \exp(i\mathbf{k} \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)) \rangle = N$$

so that

$$\Sigma_2 = \frac{N}{(2\pi)^3 V} \int |\nu(\mathbf{j})|^2 G_0(\mathbf{j}) d\mathbf{j} .$$

At the same time Σ_4 depends on

$$\langle \sum_{\alpha,\beta,\gamma,\delta} \exp(i\mathbf{l} \cdot \mathbf{R}_\alpha + i\mathbf{m} \cdot \mathbf{R}_\beta + i\mathbf{n} \cdot \mathbf{R}_\gamma + i\mathbf{p} \cdot \mathbf{R}_\delta) \rangle$$

of which the dominant terms occur when $\alpha = \beta$, $\gamma = \delta$ (the $\Sigma_2 G_0 \Sigma_2$ part) and when $\alpha = \gamma$, $\beta = \delta$ or $\alpha = \delta$, $\beta = \gamma$. These last two choices lead to terms of the form

$$\frac{N^2}{V^2} \int |\nu(\mathbf{j})|^2 |\nu(\mathbf{l})|^2 G_0(\mathbf{k} - \mathbf{j}) G_0(\mathbf{k} - \mathbf{l} - \mathbf{j}) G_0(\mathbf{k} - \mathbf{j}) d\mathbf{j} d\mathbf{l}$$

which have no poles. In this case one may show that

$$\frac{\Sigma_4}{\Sigma_2} = 0 \left(\frac{\text{Potential scattering length}}{\text{Electron wavelength}} \right) .$$

B. PERFECT ORDER

In a perfect lattice with one atom per unit cell

$$\langle \sum_{\alpha,\beta} \exp[i\mathbf{k} \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)] \rangle = \frac{N^2}{V} \frac{1}{(2\pi)^3} \sum_{\mathbf{K}} \delta(\mathbf{k} - \mathbf{K})$$

where the \mathbf{K} are the reciprocal lattice vectors. Therefore

$$\Sigma_2 = \frac{N^2}{V^2} \sum_{\mathbf{K}} \frac{|\nu(\mathbf{K})|^2}{E - \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2} .$$

The zeros of $G_0^{-1} - \Sigma_2$ then lie along the lines in E, k space illustrated by Fig. 1 in the case of one dimension.

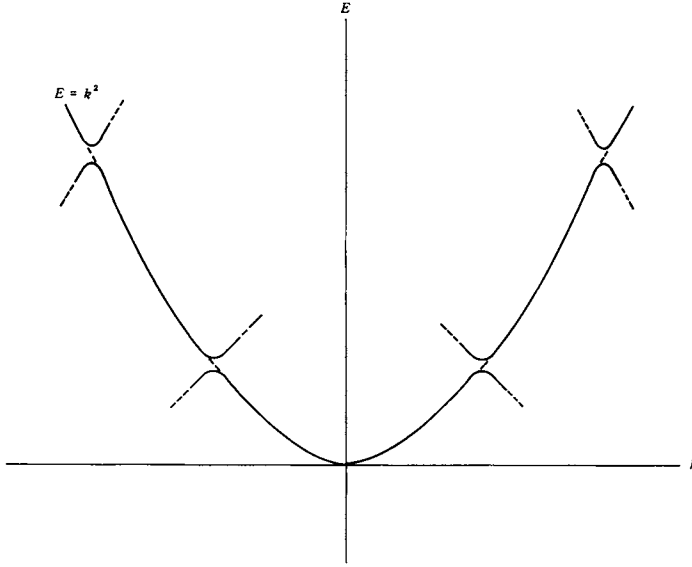


FIG. 1. One-dimensional perfect lattice.

The gaps are correct along the $E = k^2$ curve, but away from $E = k^2$ the curves are incorrect. The Σ_4 and higher terms would serve to reintroduce the periodicity in reciprocal space. It is important to note, however, that even in the case of the perfect lattice the E, k diagrams such as that given in Fig. 1 are not extended Brillouin zone pictures.

III. Polycrystalline Materials

The "geometric approximation" which makes the fourth order term $\simeq \Sigma_2 G_0 \Sigma_2$ breaks down completely in the case of a material consisting of randomly orientated perfect crystals. In this case

$$\langle \sum_{\alpha\beta} \exp[i\mathbf{k} \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)] \rangle = \frac{N^2}{V} \frac{1}{(2\pi)^3} \frac{1}{4\pi} \int d\Omega_{\mathbf{k}} \sum_{\mathbf{K}} \delta(\mathbf{k} - \mathbf{K})$$

and the term which was $\Sigma_2 G_0 \Sigma_2$ is now

$$\left[\frac{N^2}{V} \frac{1}{(2\pi)^3} \right]^2 \frac{1}{4\pi} \int d\Omega_{\mathbf{k}} \sum_{\mathbf{K}\mathbf{K}'} \delta(\mathbf{k} - \mathbf{K}) \delta(\mathbf{j} - \mathbf{K}')$$

which bears no resemblance to the $(\Sigma_2)^2$ term.

In this case and that of a liquid with true order, one must leave the angular integration (or averaging) until after the summation has been done. Thus one takes the local structure to have a certain fixed direction (the same for all parts of the liquid) and sums the series. The fixed direction is then averaged over.

There is another important point which needs to be made about the approximation. It is easy to prove that in one dimension a system of δ -functions which are such that the nearest neighbor distances are randomly distributed between $a + b$ and $a - b$ can possess gaps in their energy spectrum. The theory discussed here is not correct in those gaps — it implies a small (but finite) distribution of states in the gap.

IV. Strong Potentials

If the lattice potentials $\nu(\mathbf{r})$ are strong, and especially if they are strong enough for there to be bound states of the electrons within them, then it is useful to consider the t -function

$$t = \nu + \nu G_0 \nu + \nu G_0 \nu G_0 \nu + \dots$$

which sums the repeated scatterings off the potential. This function contains as much information as the electron propagator in the presence of the single potential; t , when considered as a function of energy, has poles at the bound state energies of ν .

In place of G for the system, one may use T which is defined in an analogous manner to t . G and T are related by

$$G(\mathbf{r}, \mathbf{r}') = G_0(\mathbf{r}, \mathbf{r}') + \int G_0(\mathbf{r}, \mathbf{r}'') T(\mathbf{r}'', \mathbf{r}''') G_0(\mathbf{r}''', \mathbf{r}') d\mathbf{r}'' d\mathbf{r}'''.$$

T possesses more of the crystal symmetries than G . Then

$$\langle G(\mathbf{k}) \rangle = G_0(\mathbf{k}) + G_0^2(\mathbf{k}) \langle T(\mathbf{k}) \rangle.$$

The origin of energy used to define $G_0(\mathbf{k})$ is of no physical significance in the infinite system and corresponding to this the effect of the first term on the right-hand side of the equation cancels with the effect of $G_0^2(\mathbf{k})$ in the second. Thus

$$\text{Im} \langle G(\mathbf{k}) \rangle = (E - \mathbf{k}^2)^{-2} \text{Im} \langle T(\mathbf{k}) \rangle .$$

The expansion of T in terms of the v_α and t_α is

$$\begin{aligned} T &= \sum_{\alpha} v_{\alpha} + \sum_{\alpha} v_{\alpha} G_0 \sum_{\beta} v_{\beta} + \dots \\ &= \sum_{\alpha} t_{\alpha} + \sum_{\alpha \neq \beta} t_{\alpha} G_0 t_{\beta} + \sum_{\substack{\alpha \neq \beta \\ \beta \neq \gamma}} t_{\alpha} G_0 t_{\beta} G_0 t_{\gamma} \dots \end{aligned} \quad (3)$$

No two consecutive t 's may have the same index. This last fact makes some of the integrals simpler since $G_0(\mathbf{x})$ is singular at the origin in (three-dimensional) coordinate space and if the potentials do not overlap the second series requires no integrations over the singular point.

V. Krönig-Penney Model

For a perfect lattice (with one atom per unit cell) the series (3) is exactly geometric. The series can now be summed in a simple manner for the potential $v(r) = -\lambda\delta(r)$ in one dimension, with lattice spacing a . This gives, if $\sigma = N/V$ and $K = 2\pi/a$

$$\begin{aligned} T(\mathbf{k}) &= \frac{-\sigma\lambda}{1 - (\lambda/2\sqrt{E}) [(\sin\sqrt{E}a)/(\cos\sqrt{E}a - \cos ka)]} \\ &= \frac{-\lambda/a}{1 + (\lambda/a) \sum_{-\infty}^{\infty} 1/[E - (k + nK)^2]} . \end{aligned}$$

The imaginary part is nonzero only when the denominator is zero, i.e.,

$$\cos ka = \cos\sqrt{E}a - \frac{\lambda}{2\sqrt{E}} \sin\sqrt{E}a .$$

This is exactly the usual expression for the Krönig-Penney model.

VI. Tight-Binding Case

When $E < 0$ the unperturbed propagator decays exponentially with increasing distance. This leads to an entirely different situation to the case when $E > 0$. This distinction does not always have a real physical foundation especially in the perfect lattice case. The decay of the propagator for $E < 0$ means that the sums in Eq. (3) are weighted toward those terms involving nearest neighbors. This corresponds exactly to tight-binding theory where the exponential decay is provided by the wave functions. One is therefore able to make a consistent approximation by retaining only a certain number of nearest neighbor terms in the sums. In particular it is easy to obtain from the series the normal tight-binding approximation.

Applying the technique to a disordered system one is able to discuss the possibility of gaps in the energy spectrum. The series (3) may be

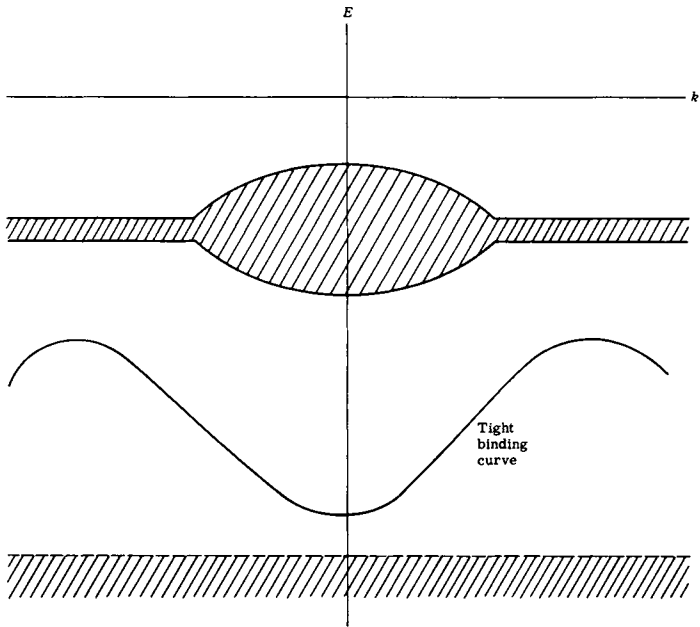


FIG. 2. Regions in which the density of states is zero.

approximately summed to give (formally)

$$T = \sum_a t_a \left(1 - \frac{\sum_{\alpha \neq \beta} t_\alpha G_0 t_\beta}{\sum_a t_a} \right)^{-1}.$$

The expression in the denominator will be given by a probability distribution in the case of a disordered system, but will be bounded, both above and below provided that the ions do not approach closer than a certain distance. This bounded property leads to the possibility of energy gaps existing in the disordered case. Thus, in one dimension, for a single level, the gap must stay open provided that the minimum distance of approach is greater than a certain value.

The shaded region in Fig. 2 shows where the density of states is identically zero. The result holds also for a single s -level in three dimensions and for the region between two s -levels in three dimensions.

VII. Three-Dimensional Problem

Beginning with the series (3), considerable progress can be made by assuming that the potential around each ion is spherically symmetric, and that the region between these spheres is at a constant potential. This means that the coordinates in the t -functions on each side of any given G_0 do not overlap. Expanding each t in terms of a real angular momentum set $Y_L(\Omega)$, enables the integrations to be carried out. This is because the G_0 are free-space propagators in the region of constant potential. Thus if one defines

$$G_{LL'} = \sum_{L''} \sum_{\mathbf{R} \neq 0} Y_{L''}(\mathbf{R}) \exp(-i\mathbf{k} \cdot \mathbf{R}) A_{L''}(R)$$

where \mathbf{R} are the interatomic distances and $A(R)$ is a product of radial functions with Clebsch-Gordon coefficients, the geometric approximation gives

$$T(\mathbf{k}) = (4\pi^2) \sum_{LL'} Y_L(\mathbf{k}) Y_{L'}(\mathbf{k}) \{t_l \delta_{ll'} + [tG(1 - tG)^{-1} t]_{LL'}\}.$$

Here the t 's are certain transforms of the t -function. In this result the dependence on the positions of the ions is entirely within G , while the

dependence on the shape of the potential is entirely within t . Thus the two effects have been separated. These remarks do not depend on the nearest neighbor approximation and are equally valid for $E > 0$ or $E < 0$.

Finally one has, if

$$F_{LL'} = G_{LL'} - i\sqrt{E} \delta_{LL'} = F_R + iF_I$$

that

$$\text{Im } T(\mathbf{k}) = (4\pi)^2 \sum_{LL'} Y_L(\mathbf{k}) Y_{L'}(\mathbf{k}) \frac{S_l(k)}{S_l(\sqrt{E})} [M]^{-1} \frac{S_{l'}(k)}{S_{l'}(\sqrt{E})}$$

where

$$M = \left(\frac{\sqrt{E}}{S} + F_R \right) F_I^{-1} \left(\frac{\sqrt{E}}{S} + F_R \right) + F_I.$$

Here S_l is a function related to $t_l(x, y)$ and is such that $S_l(\sqrt{E}) = \tan \eta_l$. This expression enables the density of states to be calculated for a disordered system. It is not immediately useful in the case of a liquid since F involves correlation functions of high order which are not known.

In the case of long range order F_I is a set of δ -functions and then M must be evaluated with particular care. The result is

$$M^{-1} = \pi \text{ cofactor} \left(\frac{\sqrt{E}}{S} + F_R \right) \delta \left(\det \left[\frac{\sqrt{E}}{S} + F_R \right] \right).$$

In the case of a perfect lattice this result is exact, the density of states being nonzero only when $\det \left[(\sqrt{E}/S) + F_R \right] = 0$. This equation for the band structure is identical to that of Kohn and Rostoker (5).

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