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THE CONCEPT OF A WAVE FUNCTION OF A DISORDERED SYSTEM

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Résumé. — Dans un système désordonné, la fonction d'onde normale Ψ est une quantité compliquée dépendant de la configuration particulière de ce système. Le calcul des quantités physiques doit être fait avant de procéder à une moyenne sur l'ensemble. On suggère la possibilité d'intervertir l'ordre du calcul et de la moyenne : ceci fait apparaître une nouvelle fonction d'onde non hermitique qui caractérise l'ensemble et peut être utilisée directement pour le calcul.

Abstract. — In a disordered system the normal wave function Ψ is a complicated quantity depending on the particular configuration. Physical quantities have to be calculated with Ψ before ensemble averaging is carried out. It is suggested that it may be possible to invert the order of calculation and averaging ; this gives rise to a new non hermitian wave function which characterizes the ensemble and can be directly used to calculate with.

1. Introduction. — Given any disordered system, S say, the calculation of any physical property is done by solving for its wave functions Ψₙ(S, E), evaluating the physical quantity concerned, A say, and finally averaging over the ensemble of S, denoted by brackets < > so that

$$\mathcal{A} = < A(S) >$$ (1.1)

For example the density of electronic states of a disordered array of atoms n(E) is related to the Green function of the Schrödinger equation which can be written in terms of the Ψ⁺:

$$(E + \frac{k^2}{2m} + i\xi + \sum \nu(r - R_\alpha) ) \Psi_\alpha(r', E) = \tau(r - r')$$ (1.2)

$$G_\alpha = \sum \Psi_\alpha^*(r, \ldots R_\alpha \ldots) \Psi_\alpha(r', \ldots R_\alpha \ldots) / (E - E_\alpha + i\xi)$$ (1.3)

$$G_\delta \equiv \text{ditto with} - i\xi$$ (1.4)

$$\rho(r, r') = \sum \Psi_\alpha^* \Psi_\alpha \delta(E - E_\alpha)$$ (1.5)

$$n(E) = \frac{1}{2\pi} \theta < G_+ - G_- > (1.6)$$

Another quantity is the conductivity (taken at T = 0)

$$\sigma_{\mu\nu} = e^2 \int < \frac{\partial \rho(X, X')}{\partial X} \frac{\partial \rho(X, X')}{\partial X'} > dX dX' / (E - E_F).$$ (1.7)

Now to actually get the set of Ψₙ is clearly impossible and to attempt to get them approximately is misguided since the physics lies in the < ρ > and < ρr > so one might as well go directly to these.

The author has discussed methods of going about this (Edwards, 1958, 1962) in the case of weak interaction. (Tight binding will be discussed in a forthcoming paper by J. L. Beeby and author.)

This paper will consist of some further discussion and speculations concerning the weak binding case. The idea behind the earlier paper is that if G⁺ is expanded in a series in U

$$U = \sum \nu(r - R_\alpha) = < \sum \nu(r - R_\alpha) >$$ (1.8)

and the series is averaged, the resulting series resembles the field theoretic expansion of electrodynamics and can be approximately summed a geometric i.e. if

$$\left( E - \frac{k^2}{2m} \sum < \nu > \right) G_0 = 1 \ldots$$

$$< G > = G_0 + < U G_0 U G_0 > + \ldots$$ (1.9)

$$\left( E - \frac{k^2}{2m} \sum < \nu > + < U G_0 U > \right) < G > \simeq 1$$ (1.10)

This means that the average motion of an electron is described by motion in the average potential < Σν > and a contribution from the fluctuations. The latter is non-hermitian and can be written A + iΔ so that if

$$< \Sigma \nu > = V$$ (1.12)

$$\left( E - \frac{k^2}{2m} V + A + i\Delta \right) < G > = 1$$ (1.13)

The expression for σμν can be rearranged in terms of < G⁺ G⁺ > etc..., and following the field theory one can expect a Bethe-Salpeter equation for < G⁺ G⁺ > :

Let the operator acting on < G > in eq. (1.10) be denoted by D. then it

$$< U(r_\alpha) U(r_\beta) > = I(r_\alpha - r_\beta)$$ (1.14)
and

\[ < G(r_1, r'_1) G(r_2, r'_2) > = G_{12} \tag{1.15} \]

\[ (D_1 D_2 + I_{12}) G_{12} \cong \delta(r_1 - r'_1) \delta(r_2 - r'_2) \tag{1.16} \]

and \( \sigma^{\mu \nu} \) can be obtained from \( G_{12} \), for random impurities for example. The above approach can be extended to include electron-electron interaction (Langer, 1962).

The important feature of the above ideas is that they are quite systematic and can be applied in three dimensions to any system. However they are inadequate in several cases for surprising as it may seem there is a much greater richness of situations in solid state theory than in quantum field theory.

2. Limitations of the field theory analogy. — The density of states in some simple cases illustrates weaknesses of the field theoretic analogy. Consider first some one dimensional cases. Firstly in the presence of a completely random potential. In this case \( V \) is a constant, and \( U \) distributed according to the functional probability

\[ P(U) \propto \text{constant} \times \exp \left[- \int U^2(r) \, d^3 r / \alpha^2 \right] \tag{2.1} \]

where \( \alpha \) is a constant. Clearly there will be fluctuations in which an arbitrary deep potential hole will occur and the electron can be in a bound state in the hole. So the density of states will be non zero from \( E = -\infty \) to \( E = +\infty \). This problem can be solved by other methods and does indeed show this feature. But eq. (1.13) for this case is

\[ < G_+ > = \left( E - \frac{\hbar^2}{2m} k^2 + V + i\alpha^2(E + V)^{-1/2} \right)^{-1} \tag{2.2} \]

and \( n(E) = 0 \) for \( E < -V \). The density \( n(E) \) has an essential singularity in \( \alpha^2 \) for \( E < -V \) (i.e. \( n(E) \propto \exp \left(-1/\alpha^2 \right) \)) and this can never be obtained from manipulations of the series (1.10). For \( E > -V \) the solution is however quite adequately expressed by (1.13), this being an asymptotic expansion.

Secondly consider a one dimensional lattice with short range order but no long range order e.g.

\[ R_n = R_{n+1} + \varepsilon_n \]

where \( |\varepsilon_n| < b \) and is uniformly probable in that range. When \( b = 0 \) there is a perfect lattice and a band structure. It has been shown by Makinson and Roberts (1962) and by Borland (1962) that the energy gaps survive for small \( b \). This result is reminiscent of those of synchronized non linear oscillator theory. On the other hand (1.13) closes the gap at once (Edwards, 1961) and agrees with the exact form only after \( b \) has exceeded a certain critical value, so that (1.13) is again too crude an approximation.

A three dimensional case requiring a more general treatment is that of a liquid metal having a mean free path comparable with the range of order in the liquid. This case may have difficulties similar to those above but there are much more evident troubles stemming from the three dimensionality of the problem. These seem fairly easy to get around (Edwards, 1962) so will not be discussed further.

As a final difficulty it must be pointed out that even if \( < G > \) can be obtained this gives no information about the character of the wave functions \( \Psi \) which go into the problem. This point is borne out by the inadequacy of \( < G > \) to give the resistance which needs \( G_{12} \) as in (1.7). It has been claimed by Mott (1962) supported by numerical assessments in the Borland, Makinson and Roberts papers that in a one dimensional random system all the states i.e. including the case \( E + V > 0 \), have an exponentially decaying form, roughly containing a factor \( \exp(-|r - R|/\Lambda) \) where \( R \) is some point in the lattice and \( \Lambda \) is of the order of the mean free path. This behaviour may go over also into three dimensions. Though it does not affect \( n(E) \) it clearly should affect the resistance and this suggests that (1.16) should be considered further.

3. The Bethe-Salpeter equation. — In quantum electrodynamics the equation (1.16) represents the motion of two electrons (or for \( G^+ G^- > \) an electron and a positron). It is not hermitian since radiation can occur, and since there are no degrees of freedom in the equation to describe this in detail it manifests itself by the term \( i\Gamma \) thus not conserving probability. However if the two electrons are far apart, then \( \Gamma \) vanishes on the energy shell \( (E = \hbar^2 k^2/2m) \) for the situation is then invariant under displacements in space and time. For the electron and positron system the interaction \( I \) is attractive and the bound state of positronium exist. To describe situations in which the emission of radiation is ignored Bethe and Salpeter introduced what has become known as a Feynman amplitude \( \Psi(r_1, r_2) \) satisfying the homogeneous form of (1.16).

\[ (D_1 D_2 + I_{12}) \Psi_{12} = 0. \tag{3.1} \]

The Green function \( G_{12} \) can be derived from a bilinear sum of \( \Psi \) as in (3.3) and the relativistic hydrogen atom and relativistic electron scattering can be investigated via \( \Psi_{12} \).

The emission and absorption of photons in the field theory is equivalent to the averaging over the fluctuations of the potential \( U \). A positive or negative fluctuation of the potential at some spot will cause an electron to be repelled from or attracted to that spot respectively; likewise another electron. So when the ensemble average has taken
place, the motion of two electrons will tend to be
the same i.e. they will behave as if attracted, to be
precise by the "potential" $I_{12}$. Some account
of the average nature of the (true) wave functions $\Psi$
is thus contained in $\mathfrak{G}_{12}$ and as has been remarked
all that needs to be known to derive transport
coefficients. This further suggests introducing
and studying the solutions of the homogeneous
equation which will be called ensemble amplitudes $\Phi$. Thus

$$(D_1 D_2 + I_{12}) \Phi_{12} = 0.$$ 

This equation will have solutions

$$\exp [\alpha (r_1 + r_2)] f(r_1 - r_2)$$

but since $D_1$, $D_2$, are not hermitian in general $a$
and $f$ will not be real or hermitian and one cannot
expect a discrete spectrum. But for $E + V < 0$
if one ignores the imaginary parts of $D_1$, $D_2$ one
can get "bound states" for suitable $I_{12}$ and $V$.
The imaginary part means that the two electrons
are only "bound" in this statistical sense, and of
course can be (really) bound in fluctuations at
different points. The conductivity however depends
critically on the nature of the $\Phi$ and for $E + V \ll 0$
it is clear physically that it will become very small.
But there doesn't really seem to be any real distinc-
tion in (3.2) between the cases $E + V < 0$
$E + V > 0$ which in (3.1) decide between bound
and unbound states. This may prove a systematic
basis for the effects predicted by Mott and Twose.
This will however require a detailed investigations
of (3.2) and the normal rules of quantum mechanics
do not apply to this equation.

The above comments were stimulated by the
conditions in liquids and in semiconductors but
certain remarks can also be made about alloys,
under these conditions in which the scattering from
individual atoms is small i.e. the pure constituents
have long mean free paths.
The density of states can be calculated from (1.6)
provided the probability of finding a particular
\textit{type} of atom on a particular site is random.
Then $V$ represents the mean lattice and $A + i\Gamma$
the effect of fluctuations. These must be included
for spurious band effects appear by using $V$ alone.
The conductivity may be calculated from (1.7).
An interesting case is when the mean free path in
the alloy is short even though that of the pure metal
is long. Equation (1.16) still can apply. Having
employed the invariance properties of the equation
it reduces to a simpler integral equation and can
be solved by the Fredholm method. Keeping only
the first approximation one has the normal result

$$\sigma = \int W_0 (1 - \cos \theta) \, d\Omega$$

but this is longer
exact in the short mean free path case and more
terms of the Fredholm solution have to be added to
give an accurate result.

**REFERENCES**


**Mott** (N. F.) and **Twose** (A.), *Advances in Physics*, 1962, 10, 107.