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Correlation of Electron Amplitudes in Impure Metals*

P. R. WEISS AND ELIHU ABRAHAMS
Physics Department, Rutgers University, New Brunswick, New Jersey

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The amplitude correlation function in an impure metal is the average over all possible arrangements of impurities of the correlation $\sum_n \psi_n^*(\mathbf{r}')\psi_n(\mathbf{r})\delta(E-E_n)$, where the ψ_n are eigenfunctions of a one-electron Hamiltonian including impurity potentials. The δ function restricts the sum to states n on the energy shell E. This quantity, whose usefulness in studies of impure metals is pointed out, is evaluated from first principles by means of multiple scattering techniques. If the impurity density is not too high, the amplitude correlation is $\rho(E)\sin[(2mE)^{\frac{1}{2}}R]\exp(-R/2\lambda)[(2mE)^{\frac{1}{2}}R]^{-1}$, where $\rho(E)$ is the density of states and $R=|\mathbf{r}-\mathbf{r}'|$.

I

ONE difficulty of a proper treatment of the effects of impurities in metals lies in the great complexity of the wave functions of the electrons in the presence of the impurities with which they interact. As a model of the metal we use a box of volume V_0 containing a dense free electron gas and N impurities at random positions $\mathbf{R}_i$ ($i=1, 2, \cdots, N$). We define one-electron wave functions in the presence of impurities. These depend very sensitively on the locations of the impurities, fluctuating widely with changes in the impurity positions. Experiments show, however, that many physical properties do not depend on the explicit values of parameters R_i but only on the concentration of the impurities, provided they are distributed at random. In order to compute the physical effects of the impurities one would be tempted, therefore, to average over all possible arrangements of the impurities.[1] Such an average carried out on the wave functions themselves is not physically meaningful because it yields the result, as in multiple scattering, that the averaged amplitude of the wave function is large only in a region whose size is measured by a mean free path, or "extinction length." This result does not correspond to the physical situation which requires the averaged probability distribution of an electron to be uniform throughout the volume V_0.

Although the averaging process must not be carried out on the wave function, there are other quantities of physical interest whose average is meaningful. One of these is the autocorrelation of the wave function

$$\psi_n^*(\mathbf{r}';\mathbf{R}_1\cdots\mathbf{R}_N)\psi_n(\mathbf{r};\mathbf{R}_1\cdots\mathbf{R}_N),$$

where $\psi_n(\mathbf{r};\mathbf{R}_1,\cdots,\mathbf{R}_N)$ is the exact one-electron wave function for the state n with the impurities at the particular locations R_i. A related quantity of interest is the sum of autocorrelations on an energy shell E. The average of this quantity is

$$g(\mathbf{r}',\mathbf{r};E)=\langle\sum_n \psi_n^*(\mathbf{r}';\mathbf{R}_1\cdots\mathbf{R}_N)\times\psi_n(\mathbf{r};\mathbf{R}_1\cdots\mathbf{R}_N)\delta(E-E_n)\rangle. \quad (1)$$

The δ function restricts the sum to the specified energy shell E and the angular brackets denote an average over all possible arrangements of the impurities. This function, which we call the amplitude correlation, has been used to study the effects of impurities on the electromagnetic properties of metals and superconductors.[2,3] Its value at $\mathbf{r}'=\mathbf{r}$, $g(\mathbf{r},\mathbf{r};E)$, is of course just the density of states at energy E. The Fourier transform yields the distribution in momentum space for the specified energy E.

In the situation where there are no impurities, the amplitude correlation is that for a free electron gas and is

$$g^0(\mathbf{r}',\mathbf{r};E)=\sum_{\mathbf{k}}\varphi_{\mathbf{k}}^*(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r})\delta(E-E_{\mathbf{k}})=\rho(E)\frac{\sin(k_0|\mathbf{r}'-\mathbf{r}|)}{k_0|\mathbf{r}'-\mathbf{r}|}, \quad (2)$$

where the $\varphi_{\mathbf{k}}(\mathbf{r})$ are plane wave functions normalized in the volume V_0, $k_0=(2mE)^{\frac{1}{2}}$, and $\rho(E)=mk_0/2\pi^2$ is the density of states at energy E. Note that we take $\hbar=1$ throughout. The effect of the impurities is to modify the amplitude correlation in a remarkably simple way:

$$g(\mathbf{r}',\mathbf{r};E)=\rho(E)\frac{\sin(k_0|\mathbf{r}'-\mathbf{r}|)}{k_0|\mathbf{r}'-\mathbf{r}|}e^{-|\mathbf{r}'-\mathbf{r}|/2\lambda}, \quad (3)$$

where λ is a "mean free path" of an electron of energy E. This result was obtained by Bardeen[2] by using a simple argument concerning the transmission of a plane wave through a slab of material containing impurities. There, λ was related to the transmission coefficient of the slab. Our purpose in this paper is to demonstrate the validity of (3) from first principles and to give the exact meaning of the mean free path λ.

The amplitude correlation cannot be obtained by treating the effects of the impurities as a small perturbation. Our procedure is one in which these effects are taken into account *to all orders*. In Sec. II we give the mathematical formulation of the amplitude corre-

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[1] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

[2] J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 274.

[3] D. Mattis and J. Bardeen [Phys. Rev. **111**, 412 (1958)] have applied the amplitude correlation to a study of the anomalous skin-effect in metals and superconductors.

lation and show how it is related to a multiple scattering problem. In Sec. III we get the amplitude correlation by means of a straightforward multiple-scattering expansion which we sum. In Sec. IV, the problem is solved by rewriting the multiple-scattering problem in such a way as to show more clearly the approximation we make. We conclude with Sec. V in which we summarize our work.

II

The total one-electron Hamiltonian in the presence of impurities may be written

$$H=K+V, \tag{4}$$

where K is the kinetic energy operator and V is the potential energy due to the impurities. We neglect the influence of the electrons upon one another except insofar as the impurity potentials are screened due to correlation effects.[4] We assume that we know how this occurs and that an effective one-electron impurity potential V is defined.

In a plane wave representation, the matrix elements of V are

$$V_{\mathbf{k}'\mathbf{k}}=\sum_i (v^i)_{\mathbf{k}'\mathbf{k}}=v_{\mathbf{k}'\mathbf{k}}\sum_i e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_i}, \tag{5}$$

where v^i is an abbreviation for $v(\mathbf{r}-\mathbf{R}_i)$, the potential due to the impurity at $\mathbf{R}_i$, and v is that due to an impurity located at the origin.

The amplitude correlation, Eq. (1), can be rewritten by the use of a Fourier transform for the energy δ function as

$$g(\mathbf{r}',\mathbf{r};E)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{iEt}\langle\textstyle\sum_n \psi_n^*(\mathbf{r}')e^{-iE_nt}\psi_n(\mathbf{r})\rangle \tag{6}$$

$$=\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{iEt}\langle\textstyle\sum_n \psi_n^*(\mathbf{r}')e^{-iHt}\psi_n(\mathbf{r})\rangle, \tag{7}$$

where we have abbreviated the wave functions in an obvious way. Equation (7) follows from (6) inasmuch as the ψ_n are eigenfunctions of H in (4). The great advantage of the form (7) is that it is a trace of the operator $\exp(-iHt)$. This can be transformed to a plane wave representation without altering its value:

$$g(\mathbf{r}',\mathbf{r};E)=\frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{iEt}\langle\textstyle\sum_{\mathbf{k}} \varphi_{\mathbf{k}}^*(\mathbf{r}')e^{-iHt}\varphi_{\mathbf{k}}(\mathbf{r})\rangle \tag{8}$$

$$=\frac{1}{2\pi}\int_{0}^{\infty} dt\, e^{iEt}\langle\textstyle\sum_{\mathbf{k}} \varphi_{\mathbf{k}}^*(\mathbf{r}')e^{-iHt}\varphi_{\mathbf{k}}(\mathbf{r})\rangle +\text{c.c.}, \tag{9}$$

where c.c. denotes the complex conjugate. Equation (7) follows from (8) since in the sum over $\mathbf{k}$ both $\varphi_{\mathbf{k}}(\mathbf{r})$ and $\varphi_{-\mathbf{k}}(\mathbf{r})=\varphi_{\mathbf{k}}^*(\mathbf{r})$ occur. The form expressed in (9) is convenient for two reasons: first, the dependence on the location of the impurities is contained only in the operator H and not in the basis functions, and second, the averaging procedure can be carried out in the plane wave representation in a particularly easy manner.

The quantity

$$\psi_{\mathbf{k}}(\mathbf{r},t)=e^{-iHt}\varphi_{\mathbf{k}}(\mathbf{r}), \tag{10}$$

which appears in (9) is recognized as the solution of the time-dependent Schrödinger equation subject to the initial condition that at $t=0$ the solution be a plane wave of propagation vector $\mathbf{k}$. The equation satisfied by $\psi_{\mathbf{k}}(\mathbf{r},t)$ is

$$i\frac{\partial}{\partial t}\psi_{\mathbf{k}}(\mathbf{r},t)-H\psi_{\mathbf{k}}(\mathbf{r},t)=i\varphi_{\mathbf{k}}(\mathbf{r})\delta(t-0), \tag{11}$$

for $t\geqslant 0$, and $\psi_{\mathbf{k}}(\mathbf{r},t)$ is to be taken as zero for $t<0$. The Fourier transform of $\psi_{\mathbf{k}}(\mathbf{r},t)$ is involved in (9). It is

$$\Psi_{\mathbf{k}}(\mathbf{r};E)=-i\int_0^{\infty} e^{iEt}\psi_{\mathbf{k}}(\mathbf{r},t)dt. \tag{12}$$

To insure convergence of the integral, E is supposed to have a small positive imaginary part which we afterward let go to zero. This also permits the inversion of (12) in an unambiguous way. The Fourier transform of (11) yields the equation satisfied by $\Psi_{\mathbf{k}}(\mathbf{r};E)$:

$$(E-H)\Psi_{\mathbf{k}}(\mathbf{r};E)=\varphi_{\mathbf{k}}(\mathbf{r}). \tag{13}$$

The operator inverse to $E-H$ is defined as $(E-H)^{-1}$, and therefore[5]

$$\Psi_{\mathbf{k}}(\mathbf{r};E)=(E-H)^{-1}\varphi_{\mathbf{k}}(\mathbf{r}). \tag{14}$$

By inserting (10) and (12) into (7), we may now express the amplitude correlation as

$$g(\mathbf{r}',\mathbf{r};E)=\textstyle\sum_{\mathbf{k}}\varphi_{\mathbf{k}}^*(\mathbf{r}')\left\langle\frac{i}{2\pi}\Psi_{\mathbf{k}}(\mathbf{r};E)\right\rangle+\text{c.c.} \tag{15}$$

Our problem is reduced to solving Eq. (14). To do this, it is convenient to use the powerful operator techniques[6] which have been developed for scattering problems. We introduce the "transition matrix" or "scattering operator" T and the "Møller wave matrix" Ω which are related to each other and to the potential by

$$\begin{aligned}&T=V+V(1/b)T=V\Omega,\\&\Omega=1+(1/b)V\Omega,\\&b=E-K.\end{aligned} \tag{16}$$

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[4] J. Friedel, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 446; N. H. March, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 1.

[5] The inverse transform of (12) is an integral along a path in the complex E plane which is parallel to and above the real axis. Along this path, $(E-H)^{-1}$ is not singular. Therefore (14) does not contain a solution of the homogeneous equation derived from (13) since such a solution belongs to a real value of E.

[6] B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950); M. Gell-Mann and M. L. Goldberger, Phys. Rev. **91**, 398 (1953).

We have defined E to have a small positive imaginary part so that Eqs. (16) are identical (except for the use of E as a complex variable rather than the incident energy) to those of a multiple-scattering problem for which the boundary conditions are that there be a plane wave incident upon a collection of scattering centers and that asymptotically the scattered waves be outgoing spherical waves. The matrix Ω carries a plane wave into the exact solution of the scattering problem.

We apply these methods to the solution of (14); using $b=E-K$, we have

$$\Psi_{\mathbf{k}}(\mathbf{r};E)=(b-V)^{-1}\varphi_{\mathbf{k}}(\mathbf{r})$$

$$=\left(\frac{1}{b}+\frac{1}{b}V\frac{1}{b}+\frac{1}{b}V\frac{1}{b}V\frac{1}{b}+\cdots\right)\varphi_{\mathbf{k}}(\mathbf{r}). \quad (17)$$

The expression (17) represents a perturbation series for $\Psi_{\mathbf{k}}(\mathbf{r};E)$ in powers of V. We have explored this expansion and have been able to sum it provided that certain multiple scattering terms can be neglected. It is simpler, however, to use the scattering operator T, and in view of its definition (16), there results

$$\Psi_{\mathbf{k}}(\mathbf{r};E)=\left(1+\frac{1}{b}T\right)\frac{1}{b}\varphi_{\mathbf{k}}(\mathbf{r}). \quad (18)$$

Alternatively, Eq. (18) can be written as

$$\Psi_{\mathbf{k}}(\mathbf{r};E)=\Omega\frac{1}{b}\varphi_{\mathbf{k}}(\mathbf{r})=\frac{1}{b_k}\Omega\varphi_{\mathbf{k}}(\mathbf{r}), \quad (19)$$

where we have made use of the fact that $1/b$ is diagonal in the plane wave representation and $1/b_k$ is a number equal to $(E-E_{\mathbf{k}})^{-1}=(E-k^2/2m)^{-1}$. In order to obtain $\Psi_{\mathbf{k}}(\mathbf{r};E)$, it is only necessary to obtain the matrix elements of T or Ω. Thus our problem is reduced to the multiple-scattering problem described by the integral equations (16). We notice that the positions of the impurities appear only in the operator T (or Ω) and that we shall therefore require averages of the matrix elements of this operator.

III

Our first method of solution involves the multiple-scattering expansion of the operator T. We define the transition matrices for the individual impurities by the operator equations

$$t^i=v^i+v^i\frac{1}{b}t^i, \quad (20)$$

where, as before, the small positive imaginary part of b specifies that contour in integrations which is appropriate for outgoing waves. The matrix elements of t^i are, in view of (5), easily shown to be of the form

$$(t^i)_{\mathbf{k}'\mathbf{k}}=t_{\mathbf{k}'\mathbf{k}}e^{-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_i}, \quad (21)$$

where t is the scattering operator for an impurity located at the origin.[7] The total scattering operator T can be expressed[8] as

$$T=\sum_i t^i+\sum_{ij}{}'' t^i\frac{1}{b}t^j+\sum_{ijl}{}'' t^i\frac{1}{b}t^j\frac{1}{b}t^l+\cdots, \quad (22)$$

where the double primes on the summations indicate that no two *adjacent* indices may be alike. We recall that T must be averaged over the possible arrangements of the locations of the impurities. To do this most conveniently, the series (22) is rearranged as follows: in any given order we separate out those terms for which a given index is the same as an earlier one and combine such terms with earlier terms having the same number of different indices. What remains is a sum over indices all of which are different. The series for T is now

$$T=\sum_i t^i+\sum_{ij}{}'\left(t^i\frac{1}{b}t^j+t^i\frac{1}{b}t^j\frac{1}{b}t^i+t^i\frac{1}{b}t^j\frac{1}{b}t^i\frac{1}{b}t^j+\cdots\right)$$

$$+\sum_{ijl}{}'\left(t^i\frac{1}{b}t^j\frac{1}{b}t^l+t^i\frac{1}{b}t^j\frac{1}{b}t^l\frac{1}{b}t^i+t^i\frac{1}{b}t^j\frac{1}{b}t^l\frac{1}{b}t^j+\cdots\right)$$

$$+\cdots. \quad (23)$$

Now the single primes on the summations indicate that all indices must be different. This expression separates T into scattering by single impurities, by pairs, by triplets, etc.[9]

To illustrate the averaging, we consider the leading term in the scattering by pairs,

$$T^{20}=\sum_{ij}{}' t^i\frac{1}{b}t^j.$$

Then, on using (21),

$$(T^{20})_{\mathbf{k}'\mathbf{k}}=\sum_{\mathbf{k}''} t_{\mathbf{k}'\mathbf{k}''}\frac{1}{b_{\mathbf{k}''}}t_{\mathbf{k}''\mathbf{k}}\sum_{ij}{}' e^{-i(\mathbf{k}'-\mathbf{k}'')\cdot\mathbf{R}_i-i(\mathbf{k}''-\mathbf{k})\cdot\mathbf{R}_j},$$

and

$$\langle(T^{20})_{\mathbf{k}'\mathbf{k}}\rangle=N(N-1)\sum_{\mathbf{k}''} t_{\mathbf{k}'\mathbf{k}''}\frac{1}{b_{k''}}t_{\mathbf{k}''\mathbf{k}}\delta_{\mathbf{k}\mathbf{k}'}\delta_{\mathbf{k}\mathbf{k}''}$$

$$=N(N-1)(t_{\mathbf{k}\mathbf{k}}{}^2/b_k)\delta_{\mathbf{k}'\mathbf{k}},$$

and one sees that only the diagonal element of T^{20} survives the averaging process. Notice that $t_{\mathbf{k}\mathbf{k}}$ is proportional to $V_0{}^{-1}$ so that if $N\gg1$, T^{20} is proportional to the square of the impurity concentration n.

The leading term in the scattering by threes is, after averaging,

$$\langle T^{30}\rangle=N(N-1)(N-2)(t_{\mathbf{k}\mathbf{k}}{}^3/b_k{}^2)\delta_{\mathbf{k}'\mathbf{k}}, \quad (24)$$

and corresponding results are obtained for the leading

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[7] J. M. Luttinger and W. Kohn, Phys. Rev. **109**, 1892 (1958), Appendix C. We are indebted to the authors for a preprint of this work.

[8] K. M. Watson, Phys. Rev. **89**, 575 (1953).

[9] See reference 7, Appendix A.

terms of higher multiple scatterings. The first correction term in the scattering by pairs is, on averaging,

$$\langle (T^{21})_{\mathbf{k}'\mathbf{k}}\rangle = N(N-1)\delta_{\mathbf{k}\mathbf{k}'}\sum_{\mathbf{k}''}\frac{|t_{\mathbf{k}\mathbf{k}''}|^2 t_{\mathbf{k}''\mathbf{k}''}}{b_{k''}{}^2}.$$

Out of the sum we can abstract the term for which $\mathbf{k}''=\mathbf{k}$ and combine it with the average of the leading term in the scattering by threes, T^{30}. This converts the number $N(N-1)(N-2)$ in (24) to $N(N-1)^2$. Having removed the term $\mathbf{k}''=\mathbf{k}$, we discard the remainder of $\langle (T^{21})_{\mathbf{k}'\mathbf{k}}\rangle$. The terms T^{22} containing four factors of t and T^{31} also containing four factors of t and repeated indices are treated in the same way. In the average, the fully diagonal terms are abstracted and combined with $\langle T^{40}\rangle$ and the remainders are discarded. This makes the factor for $\langle T^{40}\rangle$ become $N(N-1)^3$ rather than $N(N-1)(N-2)(N-3)$. We adopt this procedure for all remaining terms. In short, we preserve all multiple scatterings in the forward direction and neglect all others. We believe that the terms neglected are negligible if the density of impurities is sufficiently low that there is no overlap of the force fields of the different impurities. This criterion is easily satisfied for concentrations less than 10 atomic percent. With this approximation,

$$\langle T_{\mathbf{k}\mathbf{k}}\rangle = Nt_{\mathbf{k}\mathbf{k}} + N(N-1)\frac{t_{\mathbf{k}\mathbf{k}}{}^2}{b_k} + N(N-1)^2\frac{t_{\mathbf{k}\mathbf{k}}{}^3}{b_k{}^2} + \cdots$$

$$\cong \sum_{p=1}^{\infty}\frac{(Nt_{\mathbf{k}\mathbf{k}})^p}{b_k{}^{p-1}}. \qquad (25)$$

This is the solution to the multiple scattering problem. If we now insert (25) into (18), we find

$$\left\langle \frac{i}{2\pi}\Psi_{\mathbf{k}}(\mathbf{r};E)\right\rangle = \frac{i}{2\pi b_k}\sum_{p=0}^{\infty}\left(\frac{Nt_{\mathbf{k}\mathbf{k}}}{b_k}\right)^p \varphi_{\mathbf{k}}(\mathbf{r}). \qquad (26)$$

On using (15), we find the amplitude correlation function to be

$$g(\mathbf{r}',\mathbf{r};E) = \frac{i}{2\pi}\sum_{\mathbf{k}}\frac{1}{E-E_{\mathbf{k}}-Nt_{\mathbf{k}\mathbf{k}}}\varphi_{\mathbf{k}}{}^*(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}) + \text{c.c.} \qquad (27)$$

We separate $t_{\mathbf{k}\mathbf{k}}$ into its real and imaginary parts

$$t_{\mathbf{k}\mathbf{k}} = \mathrm{Re}(t_{\mathbf{k}\mathbf{k}}) + i\,\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}), \qquad (28)$$

and convert the sum in (27) into an integral

$$g(\mathbf{r}',\mathbf{r};E) = \frac{-(2m)^2}{\pi}\left(\frac{1}{2\pi}\right)^3\int d\mathbf{k}\,N\,\mathrm{Im}(t_{\mathbf{k}\mathbf{k}})$$

$$\times\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{[k^2+2mN\,\mathrm{Re}(t_{\mathbf{k}\mathbf{k}})-k_0{}^2]^2+[2mN\,\mathrm{Im}(t_{\mathbf{k}\mathbf{k}})]^2}, \qquad (29)$$

where we have used $\mathbf{R}=\mathbf{r}-\mathbf{r}'$ and $E=k_0{}^2/2m$. The quantity $t_{\mathbf{k}\mathbf{k}}$ in usual scattering theory is the forward scattering amplitude for a single impurity. Its imaginary part is related to the total cross section, σ, by the well-known optical theorem[10]

$$\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}) = -\frac{1}{2mV_0}k\sigma(k). \qquad (30)$$

This can be expressed in terms of a mean free path λ_k defined by

$$\lambda_k{}^{-1} = (N/V_0)\sigma(k), \qquad (31)$$

as

$$N\,\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}) = -(1/2m)(k/\lambda_k). \qquad (32)$$

In the present context, as we have pointed out, E is a variable, whereas in scattering theory the parameter E in the definition of t by Eq. (20) is fixed at the value of the energy of the incident plane wave of wave vector $\mathbf{k}$, $E_{\mathbf{k}}$. Thus, in (30) and (32), $E=k^2/2m$. In Eq. (29) the quantity involved is $t_{\mathbf{k}\mathbf{k}}(E)$, where $E=k_0{}^2/2m$, and the integration over $\mathbf{k}$ involves values of $t_{\mathbf{k}\mathbf{k}}(E)$ where $E_{\mathbf{k}}\neq E$. We can estimate the behavior of $t_{kk}(E)$ by using the first iteration of Eq. (20)

$$t_{\mathbf{k}\mathbf{k}}(E) = v_{\mathbf{k}\mathbf{k}} + \sum_{\mathbf{k}'}\frac{|v_{\mathbf{k}\mathbf{k}'}|^2}{E-E_{\mathbf{k}'}}. \qquad (33)$$

We find that if $v(\mathbf{r})$ has a finite range (as is the case due to the shielding[4]), then

$$\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}(E)) \xrightarrow[k\to\infty]{} 0,$$

and $\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}(E))$ is substantially constant for $|\mathbf{k}-\mathbf{k}_0| < 1/a$, where a is the range of the impurity potential. The first remark insures the convergence of the integral in (29) even when $R=0$. The second permits us to replace $\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}(E))$ by $\mathrm{Im}(t_{k_0k_0}(E))$ (we recall $E=k_0{}^2/2m$), provided the density of impurities is sufficiently low. The reason for this is that for low density, both the energy shift $N\mathrm{Re}(t_{\mathbf{k}\mathbf{k}}(E))$ and the width $N\,\mathrm{Im}(t_{\mathbf{k}\mathbf{k}}(E))$ will be small compared to E, which is the order of the Fermi energy. In that case, the integrand of (29) will be large only in the neighborhood of $k=k_0$. We observe that in typical cases[4] $k_0\sim 1/a$ and we therefore modify (29) by replacing $t_{\mathbf{k}\mathbf{k}}(E)$ by $t_{k_0k_0}(E)$.[11] As in (32), we have

$$\begin{aligned} N\,\mathrm{Im}(t_{k_0k_0}(E)) &= -k_0/2m\lambda_0, \\ N\,\mathrm{Re}(t_{k_0k_0}(E)) &= \Delta_0/2m. \end{aligned} \qquad (34)$$

Thus, (29) becomes

$$g(\mathbf{r}',\mathbf{r};E) = \frac{2m}{\pi}\left(\frac{1}{2\pi}\right)^3\frac{k_0}{\lambda_0}\int d\mathbf{k}\frac{e^{i\mathbf{k}\cdot\mathbf{R}}}{(k^2-k_0'^2)^2+k_0{}^2/\lambda_0{}^2}, \qquad (35)$$

where we have replaced $k_0{}^2-\Delta_0$ by $k_0'^2$. The integral is evaluated in the complex k plane in a straightforward

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[10] G. F. Chew and F. E. Low, "Scattering Theory Notes," University of Illinois, 1953 (unpublished).

[11] The conditions here are satisfied in typical cases for which $k_0\sim 1/a\sim 10^8$ cm^{-1} and for which $k_0\lambda_0\gg 1$.

manner. We get

$$g(\mathbf{r}',\mathbf{r};E)=\frac{mk_0}{2\pi^2}\frac{\sin(k_0'R)}{k_0'R}e^{-R/2\lambda_0},\tag{36}$$

which is the desired result. The meaning of λ_0 is given in (34) where it is related to the imaginary part of the forward scattering amplitude for a single impurity. The result (36) is the same as (3) if we neglect the difference between k_0 and k_0'. This difference is caused by the energy shift Δ_0 and at the Fermi level it is very small for low concentrations since it is proportional to the ratio of number densities of impurities to electrons.

We would like to call attention to the fact that the density of states at energy E is just $g(\mathbf{r},\mathbf{r};E)$ and it may be computed from (29) by setting $R=0$. In order to obtain the change in density of states due to the presence of impurities, one must carry out the integration with somewhat more care than we have given in the steps leading to (36). In our approximation, the density of states remains unchanged.

IV

In this section we shall develop the multiple scattering expansion in an alternative manner, one which is similar to methods recently proposed by Watson.[8] In order to make plausible the formal development which follows, it is necessary to review the usual treatment of multiple scattering.[12] Suppose we have a multiple-scattering problem similar to that of Eq. (16). The solution of the Schrödinger equation which we seek may be written

$$\psi(\mathbf{r})=\Omega\varphi(\mathbf{r}).$$

The usual procedure[12] is to write $\psi(\mathbf{r})$ as the sum of the incident wave $\varphi(\mathbf{r})$ and outgoing scattered waves from the impurities located at $\mathbf{R}_i$:

$$\psi(\mathbf{r})=\varphi(\mathbf{r})+\textstyle\sum_i M(\mathbf{r},\mathbf{R}_i).$$

Here, $M(\mathbf{r},\mathbf{R}_i)$ is the scattered wave from the ith impurity. If we now define $\psi^j(\mathbf{r})$ as the wave incident on impurity at $\mathbf{R}_j$, it follows that

$$\psi^j(\mathbf{r})=\psi(\mathbf{r})-M(\mathbf{r},\mathbf{R}_j).$$

However, the wave scattered from the jth impurity is related to the wave incident on the jth impurity by the scattering operator t^j,

$$M(\mathbf{r},\mathbf{R}_j)=\frac{1}{b}t^j\psi^j(\mathbf{r}),$$

where the propagator $1/b$ is again $(E-K)^{-1}$ [see Eq. (16)]. Therefore, by combining these expressions, we get the multiple-scattering equations

$$\begin{aligned}\psi(\mathbf{r})&=\varphi(\mathbf{r})+\sum_i\frac{1}{b}t^i\psi^i(\mathbf{r}),\\ \psi^j(\mathbf{r})&=\varphi(\mathbf{r})+\sum_{i\neq j}\frac{1}{b}t^i\psi^i(\mathbf{r}).\end{aligned}\tag{37}$$

If there are a large number of scattering centers randomly distributed, we attempt to solve (37) by taking an average over the positions of the impurities. Since $\psi(r)$ and $\psi^j(\mathbf{r})$ differ by only one scattering, we expect that $\langle\psi\rangle=\langle\psi^j\rangle$ to order $1/N$. Furthermore, we assume $\langle t^j\psi^j\rangle=\langle t^j\rangle\langle\psi^j\rangle\cong\langle t^j\rangle\langle\psi\rangle$. With these approximations, (37) is solved by

$$\left(1-\frac{1}{b}\sum_j\langle t^j\rangle\right)\psi(\mathbf{r})=\varphi(\mathbf{r}).\tag{38}$$

From Eq. (21), $\sum_j\langle t_{kk'}^j\rangle=Nt_{kk}\delta_{kk'}$. If we let t_c be the diagonal part of t, (38) becomes

$$\psi(\mathbf{r})=\frac{b}{b-Nt_c}\varphi(\mathbf{r}),\tag{39}$$

since matrix elements are to be taken in the plane wave representation in which b and t_c are diagonal. Now (39) may be inserted into (19), with the result

$$\langle\Psi_{\mathbf{k}}(E;\mathbf{r})\rangle=\frac{1}{b_k-Nt_{c,k}}\varphi_{\mathbf{k}}(\mathbf{r}).\tag{40}$$

Equation (40) will be recognized as identical to (26) and will therefore lead to the desired result for the amplitude correlation.

It is our purpose here to derive (40) by a more careful treatment of the multiple scattering. In so doing we will be able to see more clearly the justification of the steps leading to (38).

Our problem is again the solution of (19) which we may replace by $\psi_{\mathbf{k}}(\mathbf{r})=\Omega\varphi_{\mathbf{k}}(\mathbf{r})$. If $E=E_{\mathbf{k}}$, $\psi_{\mathbf{k}}(\mathbf{r})$ would be the outgoing-wave multiple-scattering solution of

$$(E-K-V)\psi_{\mathbf{k}}(\mathbf{r})=0.\tag{41}$$

Now the result (39) is instructive; it suggests that we try to include all forward scatterings in the "unperturbed" states so that all such "coherent" effects appear in the energy denominators as in (40). The incoherent effects would then be treated by a multiple scattering expansion. The procedure recognizes the fact that the wave will propagate with a complex propagation vector as if through a refracting medium, suffering nonforward ("incoherent") scatterings as it goes. Thus, instead of solving (41), we would try to solve the equivalent scattering problem

$$(E-K-V_c-U)\psi_{\mathbf{k}}(\mathbf{r})=0,\tag{42}$$

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[12] L. L. Foldy, Phys. Rev. 67, 107 (1945); M. Lax, Revs. Modern Phys. 23, 287 (1951).

where $U=V-V_c$; V_c is diagonal (in plane waves) and is to be chosen to contain all coherent effects. We would try to solve (42) by means of a multiple-scattering solution for the incoherent potential U.

With this discussion as a guide we return to the integral equation satisfied by the wave matrix Ω which is

$$\Omega=1+\frac{1}{b}V\Omega.$$

If we multiply both sides of this equation from the left by b and replace V by V_c+U, we get

$$(b-V_c)\Omega=b+U\Omega,$$

or

$$\Omega=\frac{1}{d}b+\frac{1}{d}U\Omega, \tag{43}$$

where the propagator $1/d=(b-V_c)^{-1}$ contains all coherent effects as we planned. Equation (43) has a simple physical interpretation[13]: The scattering is redescribed in terms of a basic set of states which are the solutions to the problem with $U=0$. These states are generated by $(1/d)b$ and they propagate through the medium with energy $K+V_c$; hence the modified propagator $1/d$. The scattering of these states is wholly incoherent and arises from the incoherent potential U. We attempt to solve (43) by means of a multiple scattering solution including incoherent effects only. To this end, guided by (37), we propose the solution

$$\begin{aligned}\Omega&=\frac{1}{d}b+\frac{1}{d}\sum_i I^i\Omega^i,\\ \Omega^j&=\frac{1}{d}b+\frac{1}{d}\sum_{i\neq j} I^i\Omega^i,\end{aligned} \tag{44}$$

where I^i is the off-diagonal part of a modified scattering operator t^i,

$$t^i=t_c{}^i+I^i=v^i+v^i\frac{1}{d}I^i. \tag{45}$$

The modification of t^i is consistent with our procedure of including all coherent effects in the propagator.[14] We now choose V_c,

$$V_c=\sum_i t_c{}^i=Nt_c. \tag{46}$$

To see if (44) is in fact a solution to (43), we insert (44), (45), and (46) into the right-hand side of (43). After some rearrangement, we find

$$\Omega=\frac{1}{d}b+\sum_i\left(1-\frac{1}{d}t_c{}^i\right)\frac{1}{d}I^i\Omega^i. \tag{47}$$

In deriving (47), we have used the fact that

$$U=\sum_i U^i=\sum_i(v^i-t_c{}^i).$$

In view of the definition of d, $1-(1/d)t_c{}^i\cong 1$ to order $1/N$, so that (47) reduces to $\Omega=\Omega$ and (44) is indeed a solution. It can now be seen that we have achieved our desired goal. We have treated coherent effects exactly to order $1/N$ and the multiple-scattering effects are described by (44) which is equivalent to

$$\Omega=\frac{1}{d}b+\frac{1}{d}\left[\sum_i I^i+\sum_{ij}{}'' I^i\frac{1}{d}I^j+\sum_{ijk}{}'' I^i\frac{1}{d}I^j\frac{1}{d}I^k\cdots\right], \tag{48}$$

where, again, no two adjacent indices are alike. All the dependence on impurity location is contained in Ω and we may now perform the usual average. At this point the great advantage of this method becomes apparent. The effect of the averaging process is to eliminate all terms in (48) for which an index appears only once. In other words, because only off-diagonal elements appear in (48), only those terms enter for which an impurity which scatters once must do so at least once again. The lowest order of (48) which survives the averaging process is the fourth since in the earlier terms every impurity cannot appear twice. We then neglect the incoherent scattering in the fourth order and we get, using the fact that b and d are both diagonal in plane waves,

$$\begin{aligned}\left\langle\frac{i}{2\pi}\Psi_{\mathbf{k}}(\mathbf{r};E)\right\rangle&=\frac{1}{b_k}\langle\Omega\rangle\varphi_{\mathbf{k}}(\mathbf{r})\cong\frac{1}{b_k}\frac{1}{d_k}b_k\varphi_{\mathbf{k}}(\mathbf{r})\\ &=\frac{1}{E-E_{\mathbf{k}}-Nt_{\mathbf{kk}}}\varphi_{\mathbf{k}}(\mathbf{r}),\end{aligned}$$

which is identical to (26) and leads in the same way to the amplitude correlation function.

V

We have derived, in Secs. III and IV, the amplitude correlation function under certain limiting conditions. One of these is that the density of impurities be sufficiently low. This insures that the energy shift due to the impurity potentials is negligible, and that the imaginary part of the scattering amplitude $t_{\mathbf{kk}}(E)$ may be replaced by $t_{k_0k_0}(E)$ as in Sec. III. In addition we have neglected certain high-order multiple-scattering terms. These are displayed most clearly in Sec. IV where they may be seen to consist of "incoherent" scatterings of the fourth order and higher. We have attempted to give an explicit evaluation of the magnitude of these terms as compared to those which we keep. We have not succeeded in doing this but we believe these terms to be small for low density. Finally, we have neglected the possibility of bound states throughout.

We have remarked that the Fourier transform of the amplitude correlation function is the distribution in k

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[13] See Gell-Mann and Goldberger, reference 6.

[14] The modified t^i differs from the usual one by a term of order $1/N$. See K. M. Watson, Phys. Rev. **105**, 1388 (1957).

for energy $E=k_0^2/2m$. When normalized, it is approximately ($k_0\lambda\gg1$)

$$(1/2\pi^2\lambda)[(k^2-k_0^2)^2+k_0^2/\lambda^2]^{-1}.$$

This shows that the eigenfunctions for energy E consist of admixtures of plane wave states with a Lorentz distribution around $k_0=(2mE)^{\frac{1}{2}}$.

We should like to point out that the mean free path λ which appears in the amplitude correlation function is not the same as that which one uses to compute the electrical resistivity due to the impurity scattering. In the latter case, a factor $1-\cos\theta$ appears in the integration over scattering angles θ in order to de-emphasize the importance of forward scatterings. The two mean free paths will be the same only in the case that the scattering is isotropic. The two are approximately equal in actual cases.

We have applied the amplitude correlation to a study of the effects of impurities on the transition temperature of superconductors.[15] Details will be published in the near future.

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[15] Lynton, Serin, and Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

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Ground-State Energy and Effective Mass of the Polaron

ELLIOTT H. LIEB, *Physics Department, University of Illinois, Urbana, Illinois*

AND

KAZUO YAMAZAKI,* *Max Planck Institut für Physik, Göttingen, Germany*

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The polaron Hamiltonian would be easily soluble were it not for the quartic term appearing therein. It is proposed to substitute for the quartic term a quadratic term having roughly the same properties, and in such a way that the ground-state energy of the new Hamiltonian is rigorously a *lower bound* for the true energy. With a very small amount of work one can obtain a lower bound as a continuous function of α for all values of α. The result agrees fairly well with the results obtained by other methods. Using the equivalent Hamiltonian one can also obtain an analytic expression for the effective mass, although one cannot say it is a bound for the true effective mass. Futhermore, once one has obtained a lower bound for the energy as a continuous function of the parameters of the Hamiltonian, one can rigorously derive upper and lower bounds for the ground-state expectation values of various operators. For example, it can be shown that for large α and large $\mathbf{k}$, $\langle a_{\mathbf{k}}{}^*a_{\mathbf{k}}\rangle\sim\mathbf{k}^{-6}$ and not $\mathbf{k}^{-2}\exp(-\mathbf{k}^2)$ as in Pekar's solution. Because of its simplicity, it is possible that this method may have application to other ground-state problems.

1. INTRODUCTION AND ILLUSTRATION

It has become common in recent years for field theorists to turn their attention to the field-theory-like problems which are to be found in solid-state theory. But rather than employing standard field-theory techniques, as might have been expected, most of the papers have tended to present entirely new methods and points of view, and have ended with the hope that the methods developed for solid-state theory may have some application to field theory. It is from this point of view that we should like to present a new method for estimating the ground-state energy E_0 and the effective mass m^* of the polaron.

It will be recalled that all the methods given so far result in an upper bound for E_0. There is Lee, Low, and Pines' weak-coupling variational calculation, as well as Pekar's variational calculation for strong coupling. There is every reason to believe that these answers are correct. Feynman[1] has shown how to use the functional integral to connect these two approximations. However, Feynman's method is rather complicated, requiring the services of the Massachusetts Institute of Technology Whirlwind computer,[2] and moreover suffers from lack of directness. It is not clear how to relate his method to more pedestrian manipulations of Hamiltonians and wave functions, although some attempts were made to fill this gap.[3] It is in fact possible to find a trial function suitable for all coupling,[4] but here again it is not clear what the changes in the trial function with coupling constant mean. Finally, although a product function such as is used for large coupling gives the asymptotic dependence of E_0 on α correctly, it yields patently wrong answers in many cases if one tries to calculate the expectation values of various operators in the ground state. As a trivial example, one obtains $\langle H^2\rangle=\infty$ with a product function.

It is not our intention to critize the variational calculations but to present an entirely different method which exploits the properties of the Hamiltonian rather than its wave function and at the same time gives a

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* On leave of absence from the Research Institute for Fundamental Physics, Kyoto, Japan.

[1] R. P. Feynman, Phys. Rev. **97**, 660 (1955).

[2] T. D. Schultz, Technical Report No. 9, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished).

[3] For example, K. Yamazaki, Progr. Theoret. Phys. (Japan) **16**, 508 (1956), and G. Höhler, Nuovo cimento **2**, 691 (1955).

[4] G. Höhler, Z. Physik **140**, 192 (1955).