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Electronic States of a Liquid Metal from the Coherent-Potential Approximation*

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A treatment of the electronic states in a liquid metal based on the coherent-potential method is given. The equations for the coherent potential and the average Green's function obtained from the requirement that the average T matrix is zero are shown to have as solutions certain expressions that were previously derived by Klauder from a different point of view. Connections with other work are mentioned.

A METHOD for calculating the one-electron states of a random substitutive alloy called the coherent potential method has been put forward by Soven[1] and has been used to treat various one- and three-dimensional alloy models by him and by Velicky, Kirkpatrick, and Ehrenreich.[2] The philosophy of this method is to immerse the scatterers in a medium specified by a potential function chosen in such a way that on the average, an electron propagating in it will undergo no further scattering upon impinging on an individual scattering center. Mathematically this requires that the average of the T matrix for a scatterer in the medium is zero, $\langle T_n \rangle = 0$. We show that this requirement for a liquid metal with no short-range order leads to equations for the coherent potential that describes the medium and for the average Green's function which can be solved in closed form. These solutions are shown to be identical with results previously derived by Klauder[3] using infinite-order perturbation theory. Our primary interest in these solutions is in the insight into the nature of the method that can be obtained from them. To study liquid metals realistically it will be necessary to include at least enough short-range order in the formalism to prevent the atoms from overlapping appreciably.

Consider a liquid metal composed of N identical scatterers in a volume Ω described by a Hamiltonian $H = H_0 + \sum_n V_n$, where H_0 is the kinetic energy operator and $\langle \mathbf{r} | V_n | \mathbf{r} \rangle = V(\mathbf{r} - \mathbf{R}_n)$. The positions of the scatterers, $\mathbf{R}_n$, are randomly distributed within Ω. Many of the properties of this system can be found from the ensemble-averaged Green's function

$$\langle G(\mathbf{k},\mathbf{k}',Z) \rangle = \Omega^{-N} \int d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_n G(\mathbf{k},\mathbf{k}',Z) ,$$

where $G(\mathbf{k},\mathbf{k}',Z) = \langle \mathbf{k} | (Z-H)^{-1} | \mathbf{k}' \rangle$, and in the last step Z approaches the energy E in such a way that the Green's functions have the proper analytic behavior. It can be shown that $G = G_0 + G_0 T G_0$, where $G_0 = (Z - H_0)^{-1}$ and

$$T = \sum_n T_n + \sum_n{}' T_n + \sum_{n,m}{}' T_n G_0 T_m + \sum_{n,m,p}{}' T_n G_0 T_m G_0 T_p + \cdots ,$$

the prime on the summation meaning that no subscript on a T can equal the one that precedes it. The T matrices for each scatterer are defined by $T_n = (1 - V_n G_0)^{-1} V_n$, and have the matrix elements

$$T_n(\mathbf{k},\mathbf{k}') = \Omega^{-1} e^{-i(\mathbf{k}-\mathbf{k}')R_n} t(\mathbf{k},\mathbf{k}') , \tag{1}$$

with

$$t(\mathbf{k},\mathbf{k}') = v(\mathbf{k}-\mathbf{k}') + (2\pi)^{-3} \times \int d\mathbf{k}_1 v(\mathbf{k}-\mathbf{k}_1) G_0(\mathbf{k}_1,Z) t(\mathbf{k}_1,\mathbf{k}') , \tag{2}$$

and $v(\mathbf{q})$ is the Fourier transform of $V(\mathbf{r})$. Inserting the T_n into G and ensemble averaging leads to an expansion for $\langle G \rangle$ in which each term is a product of $G_0(\mathbf{k},Z)$'s and $t(\mathbf{k},\mathbf{k}')$'s. The numerical factor in front of such a term, and the relations that restrict the values taken on by the internal $\mathbf{k}$'s that are summed over, arise from the process of averaging products of exponentials like the one shown in Eq. (1). A concise method for keeping track of the terms that appear in $\langle G \rangle$ is afforded by drawing a set of diagrams[3,4] that have a correspondence to these terms. The first result that comes from this process is that $\langle G \rangle$ is diagonal in $\mathbf{k}$, i.e., $\langle G(\mathbf{k},\mathbf{k}',Z) \rangle = \langle G(\mathbf{k},Z) \rangle \delta(\mathbf{k}-\mathbf{k}')$.

Klauder[3] arrived at a series of approximations to $\langle G \rangle$ by summing over ever larger class of diagrams, the highest level of approximation that he analyzed being similar in form to the Brueckner approximation of manybody theory. If the substitutions $\tau(\mathbf{k},\mathbf{k}') = v(\mathbf{k}-\mathbf{k}') + v(0) K_5(\mathbf{k}', \mathbf{k}-\mathbf{k}')$ and $S_5'(\mathbf{k},Z) = \rho v(0) \Gamma(\mathbf{k},Z)$ are made in his Eqs. (75) and (76), the approximate averaged Green's function $\Gamma(\mathbf{k},z)$ is given by

$$\Gamma(\mathbf{k},Z) = [Z - k^2 - \rho\tau(\mathbf{k},\mathbf{k})]^{-1} , \tag{3}$$

where $\rho = N/\Omega$ and

$$\tau(\mathbf{k},\mathbf{k}') = v(\mathbf{k}-\mathbf{k}') + (2\pi)^{-3} \times \int d\mathbf{k}_1 v(\mathbf{k}-\mathbf{k}_1) \Gamma(\mathbf{k}_1,Z) \tau(\mathbf{k}_1,\mathbf{k}') . \tag{4}$$

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Writing the equations in this form allows a simple comparison with the Green's function from multiple scattering theory[5] which is similar except that the quantity $\tau(\mathbf{k},\mathbf{k})$ in Eq. (3) is replaced with $t(\mathbf{k},\mathbf{k})$ from Eq. (2). The appearance of $\Gamma(\mathbf{k},Z)$ rather than $G_0(\mathbf{k},Z)$ in Eq. (4) can be called self-consistent internal propagator modification. Iterating Eq. (4) and inserting the result in Eq. (3) leads to a complicated integral equation for $\Gamma(\mathbf{k},Z)$, or inserting the expression for $\Gamma(\mathbf{k},Z)$ from Eq. (3) into Eq. (4) leads to an equation for $\tau(\mathbf{k},\mathbf{k})$.

Matsubara and Toyozawa[6] obtained an approximation for the average Green's function by a process that differs from the above in that real-space expressions and diagrams were used rather than the $\mathbf{k}$-space quantities described above. Yonezawa[7] showed the equivalence of this theory with that of Klauder and carried out a calculation for a simple three-dimensional model.

In our consideration of the coherent-potential approximation we choose to follow an algebraic development similar to the one that appears in Ref. 2 rather than considering wave functions as in the standard multiple scattering theory.[5]

The coherent potential is an initially undetermined potential field, ρw, in which on the average the electron can be considered to move according to the Green's function $\bar{G}_0=(Z-H_0-\rho w)^{-1}$. For a liquid it is reasonable to assume that the coherent potential is indendent of position because the liquid is translationally invariant on the average, but the possibility that it could depend on momentum operators must be considered. Rewriting the Hamiltonian for the system in the form $H=H_0+\rho w+\sum_n(V_n-w/\Omega)$, it can be seen that the exact Green's function can be written in terms of $\bar{G}_0$ and the scattering operators

$$\bar{T}_n=[1-(V_n-w/\Omega)\bar{G}_0]^{-1}(V_n-w/\Omega).$$

The basic postulate of this approach, that the average Green's function $\langle G\rangle$ can best be approximated by $\bar{G}_0$ if ρw is chosen so that on the average there is no further scattering from a scatterer imbedded in this field, $\langle\bar{T}_n\rangle=0$, can be described in terms of a single-site approximation.[2]

By a certain amount of algebraic manipulation of the $\mathbf{k}$-space matrix elements of $\bar{T}_n$ it can be shown that

$$\langle\bar{T}_n(\mathbf{k},\mathbf{k}')\rangle=\frac{1}{\Omega}\left(\frac{\hat{G}_0(\mathbf{k})}{\bar{G}_0(\mathbf{k})}\right)^2\left(\hat{t}(\mathbf{k},\mathbf{k})-w\frac{\bar{G}_0(\mathbf{k})}{\hat{G}_0(\mathbf{k})}\right)\delta(\mathbf{k}-\mathbf{k}'),\quad(5)$$

where

$$\bar{G}_0(\mathbf{k},Z)=[Z-k^2-\rho w]^{-1},\quad(6)$$

and

$$\hat{G}_0(\mathbf{k},Z)=[\bar{G}_0(\mathbf{k},Z)^{-1}+w/\Omega]^{-1}.$$

The quantity $\hat{t}(\mathbf{k},\mathbf{k}')$ is like the $t(\mathbf{k},\mathbf{k}')$ of Eq. (2) except that $\hat{G}_0(\mathbf{k},Z)$ takes the place of the $G_0(\mathbf{k},Z)$ in that equation. For most potential functions $V(\mathbf{r}-\mathbf{R}_n)$ it will turn out to be consistent to assume that w is not proportional to Ω, and hence $\hat{G}_0(\mathbf{k},Z)$ can be replaced by $\bar{G}_0(\mathbf{k},Z)$ in Eq. (5) as the volume Ω becomes very large. Under these circumstances it can be seen that the equation $\langle\bar{T}_n\rangle=0$ can be solved by functions $w(\mathbf{k},Z)$ and $\bar{G}_0(\mathbf{k},Z)$ that satisfy the same integral equations as $\tau(\mathbf{k},\mathbf{k},Z)$ and $\Gamma(\mathbf{k},Z)$, Eqs. (3) and (4).

This result shows that Klauder's analysis can be used to determine the level of approximation implied by the coherent-potential method in the language of perturbation theory, and that w must in general be considered a very complicated function of momentum operators as well as the energy. The latter circumstances has some interest implications when we try to think about wave functions, which, as was mentioned above, have been ignored in following the algebraic approach. If $\bar{G}_0$ was the exact Green's function for the system, then $\bar{G}_0^{-1}\psi=0$ would define the eigenstates. Plane waves satisfy this equation but the $\mathbf{k}$ vectors are complex satisfying the equation $E-k^2-w(\mathbf{k},E)=0$ for a given energy E. The average wave for a liquid should be a plane wave,[5] but since $\bar{G}_0$ is not the true Green's function for the system, it is difficult to give a meaning to the generally unnormalizable wave vectors satisfying the above equation.

Although the above argument is complete, it is reassuring to consider a simple model for which it is possible to follow continuously the process whereby the coherent potential result for an alloy goes over to Klauder's result for a liquid metal. Soven[1] first applied his method to a one-dimensional random alloy with a potential function $V(x)=-\sum_n P_n\delta(x-nd)$, where P_n equals P_A or P_B if there is an A or B atom at that site. The fraction of sites that contain A atoms is c, and the number of A atoms per unit length is $\epsilon=c/d$. If P_B is set equal to zero while c and d approach zero in such a way that ϵ remains fixed, this potential passes in the limit to a set of δ functions positioned along the x axis according to a Poisson distribution, which is a model of a liquid that was treated by Klauder.[3] Thus, the alloy calculation can be done using the coherent-potential theory and then passing to the liquid-metal limit should yield Klauder's results. In fact, this calculation already exists in the literature but it is necessary to show another connection in order to demonstrate it.

When specialized to the one-dimensional alloy model the coherent-potential method gives the same results as an average-trace method[8] which only works for one-dimensional problems. To see this we note that the coherent potential for the one-dimensional alloy is periodic, $W=-w\sum_n\delta(x-nd)$, where w will turn out to depend only on the energy. The T matrix for a scatterer immersed in this field is

$$T_n(x,x')=-[1+(P_n-w)\bar{G}_0(nd,nd)]^{-1}\times(P_n-w)\delta(x-nd)\delta(x'-nd),$$

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where $\bar{G}_0(x,x')$ is the Green's function for the electron in the field of the coherent potential. The part of this function that is needed is

$$\bar{G}_0(nd,nd)=\sin\alpha d/(2i\alpha\sin p),$$

where $\alpha=\sqrt{Z}$ and p is defined by

$$\cos p=\cos\alpha d-(w/2\alpha)\sin\alpha d.$$

The coherent-potential parameter w is determined by the equation

$$c\bar{T}_A+(1-c)\bar{T}_B=0. \tag{7}$$

The average-trace method deals with a quantity U that is a root of $dh/dU=0$, where

$$h(U)=-ip+\ln(1+U)-(1-c)\ln U. \tag{8}$$

It can be shown that setting the derivative of $h(U)$ equal to zero leads to Eq. (7) if the change of variable $U=-(w-P_A)/(w-P_B)$ is made, and the expressions for the density of states used in the two methods[1,9] also become identical.

The passage to the limit of a liquid has been carried out using the average trace method[9] and Klauder's result was obtained. In the present context this furnishes an example of passing to the limit with the coherent-potential theory.

There have been a number of other treatments of the liquid metal problem. Ziman[10] has put forward a theory of liquid metals with short-range order that he describes in terms of multiple-scattering theory.[5] He uses the quasicrystalline approximation of Lax[5] that is the same as the single-site approximation[2] when there is no short-range order, but he does not consider internal propagator modification. His work is related to the average T-matrix approximation for random alloys advanced by Korringa[11] and Beeby,[12] which also does not use internal propagator modification. Lloyd[13] does consider such modification to some extent. The work of Anderson and McMillan[14] is more closely related to the present considerations. They apply the $\langle T_n\rangle=0$ condition in a very direct way, but the scattering operator they use is not the one used here and they do not obtain the density of states function from taking the trace of a Green's function as in the theory of Klauder. They obtain a complex **k** vector for the medium that may have an origin that is similar to the one described above.

The work of Matsubara and Toyozawa[6] has been further extended in the direction of treating random alloys by several authors.[15] It has been pointed out[15] that these extensions of the Matsubara and Toyozawa theory lead in certain limits to equations that have the same form as the ones obtained by Taylor,[16] who introduced the coherent potential theory into the treatment of phonons and arrived at results that apply to electrons in the tight-binding limit. Leath[17] has discussed the connection between Taylor's equations and those that arise from the theory for phonons of Davies and Langer,[18] who patterned their work to some extent after Klauder.[3] Although these connections are related, they are not the same as the general proof shown here.

In passing we note that when Taylor's coherent-potential theory for phonons[16] is specialized to one dimension it leads to the same equations as have been obtained using the average-trace method[8] referred to above. Flinn, Maradudin, and Weiss[19] carried out some rather extensive calculations with this latter method and compared the results obtained with it to the numerical calculations of Dean[20] and the moment-trace calculations of Domb, Maradudin, Montroll, and Weiss,[21] showing in particular that it seems to represent the limit of successive approximations in the moment-trace method. These considerations also apply to the coherent potential theory.

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