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Exact Coherent Potential for Electrons in Liquid Metals[*]

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Using multiple-scattering theory, an alternative derivation is given for the coherent potential which enters the self-consistent averaged propagator which describes the motion of an electron among N stationary scatterers. The formalism represents a more straightforward approach to the problem than the usual method and allows previous results to be easily derived alongside new ones.

I. INTRODUCTION

The propagation of waves through a large number of scatterers is a problem which has been discussed many times in the literature. It has appeared in varied guises, since the underlying structure of many apparently different many-body systems is essentially the same. For example, the following different physical situations succumb to essentially the same formal multiple-scattering analysis: sound waves scattering from bubbles in a liquid, a discussion of electronic states in disordered alloys, vibrational properties of disordered solids, and electron propagation in liquid metals. Of course, each of these problems, as well as others not listed, does have its individual idiosyncrasy which makes it interesting in its own right. Nevertheless, there is a basic similarity among them and, although the emphasis of the present paper is upon the electronic states in liquid metals, it should be remembered that essentially the same techniques carry over to the other examples.

Following the early work of Edwards[1,2] we consider the model problem of an electron interacting with N stationary classical scatterers within a volume Ω. The Hamiltonian H for the system may be written down as

$$H=K_0+V=K_0+\sum_{n=1}^{N} v_n \quad , \tag{1}$$

where K_0 is the kinetic-energy operator and $\langle \vec{r}\,|v_n|\,\vec{r}\,'\rangle=\delta(\vec{r}-\vec{r}\,')v(\vec{r}-\vec{R}_n)$ is the interaction potential between the electron at $\vec{r}$ and the nth scatterer at $\vec{R}_n$. Information regarding the single-particle properties of the system is conveniently contained in the Green's function $\langle \vec{r}\,|G(z)|\,\vec{r}\,'\rangle$, which is the configuration space representation of the propagator

$$G(z)=(z-K_0-V)^{-1}\ , \tag{2}$$

where z is a complex variable. Clearly, $G(z)$ depends upon the position of all the scatterers, and in order to make contact with physical reality it is necessary to remove this dependence by performing an ensemble average

$$\langle G(z)\rangle=\int d\{\vec{R}_n\}P_n(\{\vec{R}_n\})\ G(z)\ . \tag{3}$$

Here $\{\vec{R}_n\}$ denotes a specific configuration $\{\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N\}$, $P_n(\{\vec{R}_n\})$ is the probability density for the configuration, and $d\{\vec{R}_n\}$ is the infinitesimal $3N$ dimensional volume element $d^3R_1 d^3R_2 \cdots d^3R_N$.

As an example of the utility of the ensemble averaged propagator, the density of single-particle states $N(E)$ is given by the well-known formula

$$N(E)=-\frac{1}{\pi}\lim_{\epsilon\to 0}\ \mathrm{Im}\,\mathrm{tr}\langle G(E+i\epsilon)\rangle. \tag{4}$$

The basic task is to obtain a result of the form

$$\langle G(z)\rangle=[G_0^{-1}(z)-W(z)]^{-1}\ , \tag{5}$$

where $G_0(z)=(z-K_0)^{-1}$ is the free-electron propagator and $W(z)$ is a known operator.

The standard procedure[1-3] is to derive a perturbation series formed from the iterative solution of the integral equation

$$G=G_0+G_0\ VG\ , \tag{6}$$

which follows immediately from (2) and the definition of G_0. (Here, and in the following, the explicit z dependence of the operators will be omitted for brevity where it is convenient.) Equivalently, the perturbation series in V which is implied by (6) may be reordered into the form

$$G=G_0+G_0\ T\ G_0\ , \tag{7}$$

by defining a total transition operator T for the system via $VG=TG_0$. Here we have

$$T=\sum_n t_n+\sum_{n,m}{}' t_nG_0t_m+\sum_{n,m,p}{}' t_nG_0t_mG_0t_p+\cdots \tag{8}$$

and

$$t_n=v_n+v_n G_0 t_n\ , \tag{9}$$

which is the transition operator describing the scattering from the single scatterer located at $\vec{R}_n$. The prime on the summations in (8) merely indicate that, because the t operator exactly solves the single-center problem, no subscript on a t

operator is allowed to equal the one that precedes it.

Averaging either form of the perturbation series term by term it is possible, using diagramatic techniques or otherwise, to resum selected subseries to obtain results of a similar form to (5).[1-6]

The transition operator reformulation of perturbation theory is merely an expanded form of the multiple-scattering formalism introduced by Foldy[7] and Lax.[8] In fact, as Ziman[9,10] has emphasized, useful results may be obtained by immediate approximate averaging of the compact multiple-scattering equations without recourse to infinite series. Obviously, both routes are complementary and, if the same approximations are made in the ensemble averaging, lead to the self-same destination.[5,11] However, the latter philosophy lends itself particularly well to attempts to make self-consistent calculations for the ensemble averaged propagator. Such attempts have recently led Soven[12] and Taylor,[13] within the contexts of electron states and lattice vibrations in disordered alloys, respectively, to introduce the so-called coherent potential approximation (CPA). They view a scatterer as embedded in an effective medium (the coherent potential) whose properties are decided self-consistently by choosing to allow the single center to produce no further scattering on the average.

Velický *et al.*[14] have formalized the approximation and have clearly shown that the CPA, as it is usually applied to electrons in disordered alloys, is a single-site approximation, and further, that it is the best single-site description available, a conclusion which has been verified by diagramatic analysis.[15]

Faulkner[16] has applied the single-site CPA to electronic states in liquid metals and has shown its equivalence to the most sophisticated of a series of approximations derived by Klauder,[3] who used diagrammatic techniques. However, in any realistic theory of electrons in liquid metals some account of short-range order must be made, an inclusion considered recently by Gyorffy[17] who blended the quasicrystalline approximation of Lax[18] to CPA.

It is the purpose of the present paper to introduce an exact solution for the coherent potential from which previous approximate results may be easily obtained and new ones derived. To this end, in Sec. II, the multiple-scattering formulation of CPA, essentially as given by Velický *et al.*,[14] is presented with a brief summary of previous relevant work. Section III is devoted to the derivation of an exact coherent potential and finally, in Sec. IV, we conclude with a discussion of our results and a summary.

II. COHERENT POTENTIAL

The Hamiltonian for the system (1) may be conveniently separated into two parts. We have

$$H = K + \tilde{V} , \tag{10}$$

where $K = K_0 + W$ and $\tilde{V} = V - W$. The operator W is, as yet, the unknown coherent potential which is independent of the coordinates of the scatterers $\{\vec{R}_N\}$. In a similar fashion to (6) we may write

$$G = \tilde{G} + \tilde{G}\,\tilde{V}\,G , \tag{11}$$

where

$$\tilde{G} = (z - K)^{-1} = G_0 + G_0 W \tilde{G} \tag{12}$$

is the propagator describing the electron's motion in the coherent potential. Next, a transition operator for the entire system $\tilde{T}$ may be defined by writing $\tilde{V}G = \tilde{T}\tilde{G}$, so that after averaging (11) we obtain

$$\langle G \rangle = \tilde{G} + \tilde{G}\langle \tilde{T} \rangle \tilde{G} . \tag{13}$$

Clearly, the self-consistent choice for W is made when we have

$$\langle G \rangle = \tilde{G} , \tag{14}$$

which implies [from (13)] that

$$\langle \tilde{T} \rangle = 0 . \tag{15}$$

This condition *implicitly* defines W and is the usual form of the N site CPA(NSCPA).[14]

It is now convenient to introduce a wave operator $\tilde{F}$ defined by the relation

$$G = \tilde{F}\,\tilde{G}. \tag{16}$$

Hence, from (11) and the definition of $\tilde{T}$, respectively, it follows that

$$\tilde{F} = 1 + \tilde{G} \textstyle\sum_n \tilde{v}_n \tilde{F} \tag{17}$$

and

$$\tilde{T} = \tilde{V}\tilde{F} . \tag{18}$$

Here, $\tilde{v}_n = v_n - w$, where w is merely W/N. We may now construct multiple-scattering equations by introducing the wave operator, $\tilde{\mathfrak{F}}_n$, which, acting on the wave moving in the coherent potential alone, creates the effective wave incident at the nth scatterer. The defining equation for $\tilde{\mathfrak{F}}_n$ is

$$\tilde{v}_n \tilde{F} = \tilde{t}_n \tilde{\mathfrak{F}}_n , \tag{19}$$

where $\tilde{t}_n$, in analogy with (9), is given by

$$\tilde{t}_n = \tilde{v}_n (1 + \tilde{G}\,\tilde{t}_n) , \tag{20}$$

and is the transition operator which exactly solves for the scattering of a single center located in the coherent potential at $\vec{R}_n$. Using (17), (19), and (20) to solve for $\tilde{\mathfrak{F}}_n$ gives

$$\tilde{\mathfrak{F}}_n = 1 + \tilde{G} \sum_{m \neq n} \tilde{t}_m \tilde{\mathfrak{F}}_m . \tag{21}$$

Finally, utilizing (18) and (19), Eq. (15) may be rewritten in the form

$$\langle \textstyle\sum_n \tilde{t}_n \tilde{\mathfrak{F}}_n \rangle = 0. \tag{22}$$

Equations (21) and (22) together represent a convenient multiple-scattering description of NSCPA.

An initial approximation in (21) is to take

$$\tilde{\mathfrak{F}}_n = 1 \;, \tag{23}$$

which means, by (22), that we get

$$\langle \tilde{t}_n \rangle = \frac{1}{\Omega} \int \tilde{t}_n \, d^3 R_n = 0 \,, \tag{24}$$

which is merely the condition for the extensively discussed[12–14] single-site CPA(SSCPA). Faulkner[16] has shown that in the usual "thermodynomic" limit where $N \to \infty$ and $\Omega \to \infty$, such that $N/\Omega = \rho$ (a finite density), this condition implies, in momentum representation,

$$w_{\vec{k}\vec{k}'} = \hat{t}_{\vec{k}\vec{k}'} \, \delta_{\vec{k}\vec{k}'} \;, \tag{25}$$

where

$$\hat{t} = v + v \tilde{G} \, \hat{t} \tag{26}$$

and v is the potential operator of a single scatterer located at the origin. Clearly, since the liquid metal is homogeneous, the coherent potential is diagonal in momentum space.

In order to improve over the single-site approximation we take, following Gyorffy,[17] a configurational average of Eq. (21) keeping one atom fixed, at say $\vec{R}_n$, and obtain an exact result

$$\langle \tilde{\mathfrak{F}}_n \rangle_n = 1 + \tilde{G} \langle \sum_{m \neq n} \tilde{t}_m \langle \tilde{\mathfrak{F}}_m \rangle_{mn} \rangle_n \;, \tag{27}$$

where the indices at the Dirac brackets denote which atoms are held fixed. It should be remembered that $\tilde{\mathfrak{F}}_n$ depends upon all the N coordinates $\{\vec{R}_n\}$, whereas $\tilde{t}_n$, being a single-site operator, depends only on $\vec{R}_n$. Following Lax,[18] Gyorffy closed Eq. (27) by using the quasicrystalline approximation; a method also used by Ziman,[9] and de Dycker and Phariseau[19] in the development of multiple-scattering theories without self-consistent propagator modification. The approximation is to replace $\langle \tilde{\mathfrak{F}}_m \rangle_{mn}$ by $\langle \tilde{\mathfrak{F}}_m \rangle_m$, implying that it makes little difference if we hold one or two atoms fixed while averaging (a statement which is certainly true for a perfect crystalline lattice). Taking the momentum representation of (27), after making the quasicrystalline approximation, it is a straightforward matter to prove that

$$(\langle \tilde{\mathfrak{F}}_n \rangle_n)_{\vec{k}\vec{k}'} = \tilde{\mathfrak{F}}_{\vec{k}\vec{k}'} \, e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}_n} \quad , \tag{28}$$

where

$$\tilde{\mathfrak{F}}_{\vec{k}\vec{k}'} = \delta_{\vec{k}\vec{k}'} + \sum_{\vec{k}''} \tilde{G}_{\vec{k}} \tilde{t}_{\vec{k}\vec{k}''} \tilde{\mathfrak{F}}_{\vec{k}''\vec{k}'} [S(k-k') - 1] \;. \tag{29}$$

Here, $S(k-k')$ is merely the ordinary structure factor of x-ray and neutron diffraction analysis. Gyorffy has shown that application of (28) and (29) in (22) implies, in the "thermodynamic" limit,

$$w_{\vec{k}\vec{k}'} = Q_{\vec{k}\vec{k}'} \, \delta_{\vec{k}\vec{k}'} \;, \tag{30}$$

where

$$Q_{\vec{k}\vec{k}'} = v_{\vec{k}\vec{k}} + \sum\nolimits_{\vec{k}''} v_{\vec{k}\vec{k}''} \tilde{G}_{\vec{k}''} Q_{\vec{k}''\vec{k}'} S(k'' - k') \;, \tag{31a}$$

which, using (26), may be written as

$$Q_{\vec{k}\vec{k}'} = \hat{t}_{\vec{k}\vec{k}'} + \sum\nolimits_{\vec{k}''} \hat{t}_{\vec{k}\vec{k}''} \tilde{G}_{\vec{k}''} Q_{\vec{k}''\vec{k}'} [S(k'' - k') - 1] \,. \tag{31b}$$

In the case of complete disorder, then $S = 1$ and (31b) reduces to the single-site approximation (25).

III. EXACT COHERENT POTENTIAL

A comparison of (12) with the average of (6) ensures us that if

$$W \langle G \rangle = \langle V \, G \rangle \tag{32}$$

is obeyed, then (14) is satisfied. Further, after averaging (16), in order to satisfy (14), we have

$$\langle \tilde{F} \rangle = 1 \;. \tag{33}$$

Finally, application of (14) and (16) with (32) gives

$$W = \langle V \, \tilde{F} \rangle \,. \tag{34}$$

It should now be emphasized that (15) and (32)–(34) are all completely equivalent statements ensuring the self-consistency relation (14). It is reasonable to assume that the last form [Eq. (34)] will prove most useful since it *explicitly*[20] defines the coherent potential.

In passing we note that (34) is, in a formal sense, very similar to the "level shift operator" and "optical model potential" of nuclear scattering theory.[21]

Clearly, we could use the expressions given by (19)–(21) in (34) to construct a multiple-scattering formalism for W. However, in order to ensure that major contributions to the coherent potential are included in the first few terms of the multiple-scattering series, it is better to start by defining the propagator introduced by Faulkner[16] as

$$\hat{G} = (\tilde{G}^{-1} + w)^{-1} \;. \tag{35}$$

Such an operator describes the average propagation of the electron among $(N-1)$ scatterers. The transition operator $\hat{t}_n$,[22] which then best solves for the average scattering from a single center located in the midst of $(N-1)$ other scatterers, is given by

$$\hat{t}_n = v_n \, (1 + \hat{G} \, \hat{t}_n) = v_n \hat{f}_n \;. \tag{36}$$

Further, a wave operator $\hat{\mathfrak{F}}_n$, describing a wave propagating in the coherent potential and being scattered by all centers except the nth, is conveniently defined via the relation

$$\tilde{F} = \hat{f}_n \, \hat{\mathfrak{F}}_n \;. \tag{37}$$

Then, eliminating $\tilde{F}$ between (17) and (37) by using (36) gives, after some algebra,

$$\hat{\mathfrak{F}}_n = \hat{G}\tilde{G}^{-1}\left[1+\tilde{G}\sum_{m\neq n}(v_m - w)\,\hat{f}_m\hat{\mathfrak{F}}_m\right]. \tag{38}$$

In the usual "thermodynamic" limit, if $v(\vec{r}-\vec{R}_n)$ is reasonably well localized around $\vec{R}_n$ like a screened ionic potential in a liquid metal, we have $\hat{G}\to\tilde{G}$. Hence, (38) becomes

$$\hat{\mathfrak{F}}_n = 1+\tilde{G}\sum_{m\neq n}\bar{t}_m\hat{\mathfrak{F}}_m\,, \tag{39}$$

where

$$\bar{t}_m = \tilde{v}_m + \tilde{v}_m\tilde{G}\,\hat{t}_m \tag{40}$$

and $\hat{t}$ is given by (26).

Finally, substituting (36) and (37) in (34), we have

$$W = \langle \textstyle\sum_n \hat{t}_n\hat{\mathfrak{F}}_n\rangle\,, \tag{41}$$

which, with (39), constitutes the main formal result of this paper and represents an alternative to the usual formulation [Eqs. (21) and (22)] of NSCPA.

IV. DISCUSSION AND SUMMARY

In analogy with (23) the zeroth approximation in (41) is to take $\hat{\mathfrak{F}}_n = 1$, which immediately recovers the usual single-site result [Eq. (25)].

Clearly by expansion of the expression (39) for $\hat{\mathfrak{F}}_n$, results to any order may be constructed, though high-order structural correlations are soon required for the necessary ensemble averaging. It is more instructive to use the usual quasicrystalline approximation which correctly includes all pair correlations and approximates those of higher order. The resulting equations have exactly the same form as (28) and (29), but with $\tilde{\mathfrak{F}}$ and $\tilde{t}$ replaced by $\hat{\mathfrak{F}}$ and $\bar{t}$. Hence, we have, finally,

$$w_{\vec{k}\vec{k}'} = (\hat{t}\hat{\mathfrak{F}})_{\vec{k}\vec{k}'}\,\delta_{\vec{k}\vec{k}'}\,, \tag{42}$$

where

$$(\hat{t}\,\hat{\mathfrak{F}})_{\vec{k}\vec{k}'} = \hat{t}_{\vec{k}\vec{k}'} + \textstyle\sum_{k''}\hat{t}_{\vec{k}\vec{k}''}\tilde{G}_{\vec{k}''}(\bar{t}\,\hat{\mathfrak{F}})_{\vec{k}''\vec{k}'}[S(k''-k')-1]. \tag{43}$$

The result of Gyorffy [Eq. (31b)] is recovered if we make $\bar{t}=\hat{t}$, an equality which, by (40), is certainly not true in general. The main feature of $\bar{t}$ is that it is essentially a measure of the deviation of the single-site scattering from the average which is given by $\hat{t}$. This implies that the single-site term in the exact expression for the coherent potential is the major contributor, and higher multiple-scattering corrections merely take care of fluctuations from this main term. This character would be completely lost in the approximate result (43) if the above equality were used.

In summary, then, using multiple-scattering theory an exact result is derived for the self-consistent coherent potential which appears in the averaged propagator of an electron moving in the potential field of N stationary scatterers [Eqs. (39) and (41)]. The formalism represents an alternative, and possibly more convenient, explicit[20] description of the situation to the equivalent, but implicit formulation which is normally used [Eqs. (21) and (22)]. The usual single-site approximation [Eq. (25)] is quickly obtained from the exact expression for the coherent potential and terms involving higher-order structural correlations may be included merely by taking more terms in the multiple-scattering series. In particular, an explicit result using the quasicrystalline approximation is derived in an attempt to include the effects of short-range order via the pair correlation function, or more strictly, the related structure factor. A similar structural approximation is used by Gyorffy[17] and, as he points out, in the limit of perfect order it is exact and the theory reduces to the band structure calculation of Korringa,[23] Kohn and Rostoker.[24] While in the opposite limit (perfect disorder) the single-site approximation[14] is recovered. It is suggested that, on intuitive grounds, the approximate result, including short-range order presented here, may be more useful than that of Gyorffy. Of course, actual numerical calculations would be necessary to check this surmise. Unfortunately, the very feature which makes the CPA so useful, that is, its self-consistency, also makes numerical work lengthy and tedious, and to date no such calculations including structural correlations exist.

It is hoped that the present method will be applied in a future publication to the effects of order on the electron states in binary alloys using the structure factors recently introduced by Bhatia and Thornton.[25,26]

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[22] The same symbol is used here for the transition operator as in Eq. (26), for obvious reasons. In order to aid the reader with the proliferating notation we briefly summarize here the loose physical meaning associated with, for example, the symbols derived from the arbitrary operator A, namely, $\hat{A}$ and $\tilde{A}$. Respectively, these denote A operating in free space, in the coherent potential created by $N-1$ scatterers, and in the coherent potential created by N scatterers.

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First-Principles Full-Zone $\vec{k}\cdot\vec{p}$ Extrapolations Critically Evaluated[*]

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The extrapolation technique that results from using calculated velocity matrix elements to couple a first-principles band calculation at Γ with a $\vec{k}\cdot\vec{p}$ expansion for mapping out energy bands over the entire zone is critically explored. Results for Bi, PbTe, and Al are discussed. The crucial finding is that the extent to which the $\vec{k}\cdot\vec{p}$ results correctly solve the eigenvalue problem is due to a fortuitous cancellation between states omitted in the truncation. Consequently, a significant augmentation of the $\vec{k}\cdot\vec{p}$ expansion set can produce little improvement. Results of orthogonalized-plane-wave calculations for PbTe are compared with existing augmented-plane-wave results, with excellent agreement in the nonrelativistic case. It is also found that relativistic band calculations by the double-expansion technique need more intermediate (nonrelativistic) basis states than were used in the PbTe work.

I. INTRODUCTION

The idea of coupling a first-principles band calculation, including velocity matrix elements at a single point in the Brillouin zone with a $\vec{k}\cdot\vec{p}$ extrapolation to map out the energy bands over the entire zone, has been explored recently by a large number of workers.[1-11] Since the $\vec{k}\cdot\vec{p}$ expansion[12] is exact until truncation, it is particularly appealing as a technique for inexpensively extrapolating not only first-principles energies, but also wave functions (and, hence, matrix elements, charge densities, etc.). Many properties now being calculated require some integral of the wave functions over the Brillouin zone. Brinkman and Goodman[1] used this technique to obtain the valence charge density in performing a self-consistent orthogonalized-plane-wave (OPW) calculation for Si. Trickey and Conklin[8] proposed a self-consistent augmented-plane-wave (APW) technique, starting from this ansatz, that simultaneously avoids iterating the APW calculation and removes the muffin-tin restriction without actually doing a non-muffin-tin APW calculation. Parada and Pratt[3-5] used the combined APW $\vec{k}\cdot\vec{p}$ technique to treat the PbTe vacancy problem in the Wannier representation. The optical constants for PbTe were calculated by Buss and Parada,[6] and a similar calculation was attempted by the present author for Bi.[9] Results[2-6] on PbTe led a number of workers to attempt other materials.[7,9-11] These latter calculations were consistently less than satisfactory. The utility of the techniques is obviously dependent on the faithfulness of the calculated wave functions. The purpose of this paper is to explore the limitations of full-zone $\vec{k}\cdot\vec{p}$.

Several workers have recognized the inadequacies for materials in which the d bands[7,11] are important. Kuebbing *et al.*[7] examined TiC and found the $\vec{k}\cdot\vec{p}$ convergence very poor (discrepancies up to 8 eV) for the relevant d levels. They then carefully reexamined PbTe and found that, while they could reproduce the original results (which had discrepancies up to 1 eV), even doubling the $\vec{k}\cdot\vec{p}$ basis did not significantly improve the energy level agreement. Williams[11] also found full-zone $\vec{k}\cdot\vec{p}$ lacking