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Note on Impurity Bands

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The density of states of a random array of attractive potentials is studied in the impurity-band regime by double-time Green's functions. Statistical correlations are built in at the same level as the quantum-mechanical correlations, and a detailed treatment of pair effects is given. The method is shown to be equivalent to the self-propagator techniques of Des Cloizeaux.

I. INTRODUCTION

Recently there has been considerable effort expended in trying to understand the electron density of states due to a random array of attractive potentials. In one dimension, particularly, we have obtained a rather complete physical picture for the entire range of impurity concentrations.[1-3] In three dimensions our understanding, needless to say, is not so complete.[1]

A particularly satisfactory diagrammatic scheme for the low-density regime was introduced a few years ago by Des Cloizeaux.[4] Using a novel diagrammatic expansion in which he introduces the idea of a "self-propagator," he obtained a cluster-like expansion of the Green's function. Direct comparison between the density of states obtained by this method in one dimension and a numerically exact density of states revealed excellent agreement for energies greater than four times the binding energy of the impurity.

It is the aim of this paper to present an alternate approach to this problem which we believe is basically equivalent to the "self-propagator" technique and which we hope will help elucidate it.

II. GREEN'S FUNCTION

The Hamiltonian we study is

$$\mathcal{H}=\sum_{\vec{k}} \epsilon_{\vec{k}} a_{\vec{k}}^{\dagger} a_{\vec{k}} - V \sum_{\vec{k},\vec{k}'} a_{\vec{k}}^{\dagger} a_{\vec{k}'} \rho(\vec{k}-\vec{k}') \quad , \tag{1}$$

where $a_{\vec{k}}^{\dagger}(a_{\vec{k}})$ creates (destroys) an electron with energy $\epsilon_{\vec{k}}$ and momentum $\vec{k}$ and

$$\rho(\vec{q})=(1/V)\sum_i e^{-i\vec{q}\cdot\vec{R}_i} \quad , \tag{2}$$

where $\vec{R}_i$ is the position of impurity i and V is the volume.

Introducing the double-time Green's function[5]

$$\mathcal{G}_{\vec{k}\vec{k}'} \equiv \langle\langle a_k ; a_{\vec{k}'}^{\dagger} \rangle\rangle \quad , \tag{3}$$

one finds that it satisfies

$$(\omega-\epsilon_{\vec{k}})\mathcal{G}_{\vec{k}\vec{k}'} = \frac{\delta_{\vec{k}\vec{k}'}}{2\pi} - v\sum_{\vec{l}_1} \rho(k-l_1)\mathcal{G}_{\vec{l}_1,\vec{k}'} \quad . \tag{4}$$

We need to know the last term in (4) so we write our equation for it

$$\sum_{\vec{l}_1} \rho(\vec{k}-\vec{l}_1)\mathcal{G}_{\vec{l}_1,\vec{k}'} = \frac{\rho(\vec{k}-\vec{k}')}{2\pi(\omega-\epsilon_{\vec{k}'})} - v\sum_{\vec{l}_1,\vec{l}_2} \frac{\rho(\vec{k}-\vec{l}_1)}{\omega-\epsilon_{\vec{l}_1}} \rho(\vec{l}_1-\vec{l}_2)G_{\vec{l}_2\vec{k}'} \tag{5}$$

$$= \frac{\rho(\vec{k}-\vec{k}')}{2\pi(\omega-\epsilon_{\vec{k}'})} - vF(\omega)\sum_{\vec{l}_2} \rho(\vec{k}-\vec{l}_2)\mathcal{G}_{\vec{l}_2\vec{k}'} - v\sum_{\vec{l}_1} \rho_1(\vec{k},\vec{l}_1;\omega)\mathcal{G}_{\vec{l}_1,\vec{k}'} \quad , \tag{6}$$

where

$$\rho_1(\vec{k},\vec{k}';\omega) \equiv \frac{1}{L}\sum_{i_1\neq i_2} \exp(-i\vec{k}\cdot\vec{R}_{i_1} + i\vec{k}'\cdot\vec{R}_{i_2})$$

$$\times \frac{1}{L}\sum_{\vec{l}_1}\frac{\exp[i\vec{l}_i(\vec{R}_{i1}-\vec{R}_{i2})]}{\omega-\epsilon_{\vec{l}_1}} \qquad (7a)$$

$$=\frac{1}{L}\sum_{i_1\neq i_2}\exp(-ikR_{i_1}+ikR_{i_2})F(\omega)$$

$$\times\exp(i\omega^{1/2}|R_{i_1}-R_{i_2}|) \qquad (7b)$$

and

$$F(\omega)\equiv(1/L)\textstyle\sum_k 1/(\omega-\epsilon_k)=1/2i\omega^{1/2}\ . \qquad (8)$$

We have specialized to one dimension so that we can make contact with the work of Des Cloizeaux. As can be seen, generalization to three dimensions involves no major difficulties.

Rewriting (7b) we obtain

$$[1+vF(\omega)]\sum_{l_1}\rho(k,l_1;\omega)\mathcal{G}_{l_1,k'}=\frac{\rho_1(k,k';\omega)}{2\pi(\omega-\epsilon_{k'})}-v\sum_{l_1}\rho_1(kl_1;\omega)\mathcal{G}_{l_1,k'}\ . \qquad (9)$$

Continuing in this fashion we can obtain a hierarchy of equations

$$[1+vF(\omega)]\sum_{l_1}\rho_n(k,l_1;\omega)\mathcal{G}_{l_1,k'}=\frac{\rho_n(kk';\omega)}{2\pi(\omega-\epsilon_{k'})}-v\sum_{l_1}\rho_{n+1}(kl_1;\omega)\mathcal{G}_{l_1,k'}\ , \qquad (10)$$

with

$$\rho_n(k,k';\omega)=F^n(\omega)\frac{1}{L}\sum_{i_1\neq i_2;\,i_2\neq i_3;\,i_n\neq i_{n+1}}\exp(-ikR_{i_1}+ik'R_{i_{n+1}})\exp[i\omega^{1/2}(|R_{i_1}-R_{i_2}|+\cdots+|R_{i_n}-R_{i_{n+1}}|)]\ . \qquad (11)$$

One can obtain a formal perturbation theoretic solution to (10) for $G_{kk'}(\omega)$:

$$\mathcal{G}_{kk'}(\omega)=\frac{1}{2\pi}\left(\frac{\delta_{kk'}}{\omega-\epsilon_k}+\frac{t(\omega)}{(\omega-\epsilon_k)^2}\sum_{n=0}^{\infty}t^n(\omega)\rho_n(k,k';\omega)\right)\ , \qquad (12)$$

where

$$t(\omega)=-v/[1+vF(\omega)] \qquad (13)$$

is the impurity t matrix.

III. AVERAGING

The problem now is to calculate the configuration-averaged Green's function $\langle\mathcal{G}_{kk}(\omega)\rangle$. This means we need to know $\langle\rho_n(k,k;\omega)\rangle$ for all n.

Rearranging (11) one finds

$$F^{-n}(\omega)\rho_n(k,k;\omega)=\rho(1,2)\rho(2,3)\cdots\rho(n,n+1), \qquad (14)$$

where

$$\rho(1,2)=\exp(-ikR_{i_1})\exp(i\omega^{1/2}|R_{i_1}-R_{i_2}|)\exp(ikR_{i_2}) \qquad (15)$$

and we have suppressed the (k,ω) indexes as well as the sums on $(1,2,\ldots,n+1)$. The simplest approximation one can make for $\langle\rho_n(k,k;\omega)\rangle$ is

$$\langle\rho_n(k,k;\omega)\rangle=F^n(n)\langle\rho(1,2)\rangle\langle\rho(2,3)\rangle\times\langle\rho(3,4)\rangle\cdots\langle\rho(n,n+1)\rangle\ . \qquad (16)$$

This is equivalent to assuming there is no interference between scattering events on different sites and leads to

$$\langle\rho_n(k,k;\omega)\rangle=\frac{c^{n+1}}{(\omega-\epsilon_k)^n}\qquad(n=1,\ldots)\ ,$$
$$\langle\rho_0(k,k;\omega)\rangle=c\ , \qquad (17)$$

and

$$\langle\mathcal{G}_{kk}(\omega)\rangle=\frac{1}{2\pi}\left(\frac{1}{\omega-\epsilon_k-ct(\omega)}\right)\ . \qquad (18)$$

This is an old result which has been discussed adequately elsewhere.[4] It predicts an impurity band, but of distinctly the wrong shape.

The next simplest approximation we can make for $\langle\rho_n(k,k;\omega)\rangle$ can be motivated as follows: The averaging procedure in (16) would be exact if all the indexes $(1,\ldots n)$ where restricted to be unequal rather than only unequal in pairs, e.g., $1\neq2$, $2\neq3$, etc. Now the fact that we built into our derivation of $\mathcal{G}_{kk'}(\omega)$ the pairwise inequality bought us, so to speak, t-matrix scattering instead of bare potential scattering. If we could build into ρ_n the ternary restrictions $(1\neq2,\ 2\neq3,\ 3\neq1)$; $(2\neq3,\ 3\neq4,\ 4\neq2)$; etc., we would have an adequate treatment of pair effects. This can be effected without much effort. Consider first,

$$\rho_2(k,k;\omega)=\sum_{i_1\neq i_2;\,i_2\neq i_3}\rho(1,2)\rho(2,3)$$

$$= \sum_{(i_1 \neq i_2 \neq i_3)} \rho(1,2)\rho(2,3) + \sum_{i_1 \neq i_2} \rho(1,2)\rho(2,1) \quad , \tag{19}$$

where $(i_1 \neq i_2 \neq i_3)$ means the inequality holds among all pairs. Then,

$$\langle \rho_2 \rangle = \langle \rho(1,2) \rangle \langle \rho(2,3) \rangle + \langle \rho(1,2)\rho(2,1) \rangle \quad . \tag{20}$$

For $\rho_3(k,k;\omega)$ we write

$$\rho_3(k,k;\omega) = \sum_{(i_1 \neq i_2 \neq i_3);\,(i_2 \neq i_3 \neq i_4)} \rho(1,2)\rho(2,3)\rho(3,4)$$

$$+ \sum_{(i_1 \neq i_2 \neq i_4)} \rho(1,2)\rho(2,1)\rho(1,4)$$

$$+ \sum_{(i_1 \neq i_2 \neq i_3)} \rho(1,2)\rho(2,3)\rho(3,2)$$

$$+ \sum_{(i_1 \neq i_2)} \rho(1,2)\rho(2,1)\rho(1,2) \quad . \tag{21}$$

Then averaging

$$\langle \rho_3 \rangle = \langle \rho(1,2) \rangle \langle \rho(2,3) \rangle \langle \rho(3,4) \rangle$$

$$+ \langle \rho(1,2)\rho(2,1) \rangle \langle \rho(1,4) \rangle$$

$$+ \langle \rho(1,2) \rangle \langle \rho(2,3)\rho(3,2) \rangle$$

$$+ \langle \rho(1,2)\rho(2,1)\rho(1,2) \rangle . \tag{22}$$

As can be seen from above, our scheme is to build in terniary restrictions and with those built in to factorize our averages. For ρ_2 this procedure is sufficient to yield the exactly averaged ρ_2 while for ρ_3 we obtain an incorrectly averaged first term in (21) because we have failed to build in the restriction $i_1 \neq i_4$. Notice that if we had built this term in we would have to add to ρ_3 the term $\rho(1,2)\rho(2,3)\rho(3,1)$, which represents the first contribution to three impurity scattering events.

The errors we make with the above factorization scheme in higher-order ρ's correspond to our neglect of three and more impurity clustering effects.

Defining g_n as

$$g_n(\omega,k) = \langle \rho(1,2)\rho(2,1)\rho(1,2)\cdots \rangle F^n(\omega) \quad (n \text{ factors})$$

$$= R_n(\omega,k) F^n(\omega) \quad , \tag{23}$$

we show the result of calculating $\langle \rho_n \rangle$ for $n = 1-5$ in Table I. Each succeeding row in the table corresponds to a higher value of concentration c. Examination of the table row by row suggests that the sum of the terms in the second row is just the square of the terms in the first row. Examination

TABLE I. Coefficients $\langle \rho_n \rangle$ in the expansion of the average Green's function in powers of the one-impurity t matrix, are decomposed in powers of the concentration. The sums are then performed row by row. See the text for the definition of g_n.

	c^2	c^3	c^4	c^5	c^6
$\langle \rho_1 \rangle =$	g_1				
$\langle \rho_2 \rangle =$	g_2	$+g_1^2$			
$\langle \rho_3 \rangle =$	g_3	$+2g_1g_2$	$+g_1^3$		
$\langle \rho_4 \rangle =$	g_4	$+2g_1g_3+g_2g_2$	$+3g_2g_1^2$	$+g_1^4$	
$\langle \rho_5 \rangle =$	g_5	$+2g_1g_4+2g_2g_3$	$+3g_3g_1^2+3g_2^2g_1$	$+4g_1^3g_2$	$+g_1^5$

of the simple combinative problem suggested by Table I convinces one that the nth-row sum is just the nth power of the first-row sum. What we wish to calculate is, of course,

$$\sum_{n=0}^{\infty} t^n \langle \rho_n \rangle \quad .$$

Referring again to Table I, this can be written in the pair approximation as

$$\sum_{n=0}^{\infty} t^n \langle \rho_n \rangle = c + c^2 \sum_{r=1}^{\infty} t^r g_r + c^3 \left(\sum_{r=1}^{\infty} t^r g_r \right)^2 + \cdots$$

$$+ c^{n+1} \left(\sum_{r=1}^{\infty} t^r g_r \right)^n + \cdots$$

$$= c \Big/ \left(1 - c \sum_{r=1}^{\infty} t^r g_r \right)$$

$$= c \Big/ \left(1 - c \sum_{r=1}^{\infty} \tilde{t}^r R_r \right) \quad , \tag{24}$$

with

$$\tilde{t} = t(\omega) F(\omega) \quad . \tag{25}$$

Using (12) and (24)

$$\langle \mathcal{G}_{kk}(\omega) \rangle = (2\pi)^{-1} \left[(\omega - \epsilon_k)^{-1} + (\omega - \epsilon_k)^{-2} c t(\omega) \Big/ \left(1 - c \sum_{r=1}^{\infty} \tilde{t}^r R_r \right) \right] \quad . \tag{26}$$

Now

$$\sum_{r=1}^{\infty} \tilde{t}^r R_r = B(k,\omega) + A(\omega) \quad , \tag{27}$$

where

$$A(\omega) = \sum_{n=1}^{\infty} R_{2n} \tilde{t}^{2n} = \frac{1}{L} \int dx\, dx' \, 1 - \tilde{t}^2 \, \frac{\exp(2i\omega^{1/2}|x-x'|)}{1 - \tilde{t}^2 \exp(2i\omega^{1/2}|x-x'|)} \quad , \tag{28}$$

$$B(k,\omega)=\sum_{n=0}^{\infty} R_{2n+1}\tilde{t}^{2n+1}=\frac{1}{L}\int dx\,dx'\,1-\tilde{t}^{2}\ \frac{\exp[i\omega^{1/2}|x-x'|-ik(x-x')]}{1-\tilde{t}^{2}\exp(2i\omega^{1/2}|x-x'|)}\ . \tag{29}$$

The integrals in (28) for $A(\omega)$ may be performed explicitly, yielding

$$A(\omega)=(i\omega^{1/2})^{-1}(\ln\omega^{1/2}+\ln\omega^{1/2}-2i+2\ln\omega^{1/2}-i)\ , \tag{30}$$

where we have used (8) and (13).

While a formal expansion for $B(k,\omega)$ can be obtained by expanding the denominator of the integrand in (29) and then performing the integration:

$$B(k,\omega)=2i\sum_{n=0}^{\infty}\tilde{t}^{(2n+1)}\frac{(2n+1)\omega^{1/2}}{(2n+1)^{2}\omega-k^{2}}\ . \tag{31}$$

Comparing $\langle \mathcal{G}_{kk}(\omega)\rangle$ given in (26) using (30) and (31) with a similar expression of Des Cloizeaux shows that the two approaches yield identical results in this approximation.[6]

An explicit comparison is made in Des Cloizeaux's paper with the density of states calculated numerically and that calculated from (27) and he found rather good quantitative agreement between the shapes of impurity band calculated both ways.

A systematic expansion of the t matrix building in higher and higher statistical correlations is in principle possible. These terniary and higher clusters enables one to calculate the tails of the impurity band below the two-impurity electron binding energy at which the present density of state cuts off. The main feature of this expansion is that the statistical correlations are treated at the same level as the quantum-mechanical correlations. This means building in binary statistical correlations at the same time treating exactly quantum-mechanical electron-impurity pair interactions. In the work on Des Cloizeaux this procedure is accomplished by means of his articulation points, which separate statistically events before and after a particular cluster expansion by requiring that all impurities the electron meets before an articulation point is different from those it meets afterwards.

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[6]There is a factor of $1/\pi$ difference in our definition of $G_{kk'}$ and Des Cloizeaux's. In addition there appears to be a typographical misprint in Ref. 4 in going from Eq. (22) to (23).

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Sign of the Hall Effect for Hopping Transport in Molecular Crystals*

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It is shown that the Hall effect for hopping transport may be anomalous in sign, just as it may be for coherent transport in narrow bands. Anthracene is treated as a specific example.

It has been recognized for some time that charge carrier transport in semiconductors with narrow bands (with widths of order kT or less) may give rise to an anomalous (negative) Hall effect.[1,2] In such a solid, the carriers are deflected in a direction opposite to the Lorentz force. For this to happen, the band must be not only narrow but also unsymmetrical. In a narrow band, all levels are almost equally populated, so that states with negative effective mass contribute on almost equal terms with states with positive effective mass. In the Hall effect, each effective-mass contribution is weighted according to the velocity of the carrier in that state, which depends on the band structure. If the band is unsymmetrical, the various contributions receive unequal weights and the negative effective-mass contributions may dominate, leading to a negative Hall effect.

It is also well known that for sufficiently narrow bands hopping, i.e., random incoherent transfer to neighboring sites, may be a more appropriate description of transport than coherent motion in a band,