

THE ELECTRONIC STATES OF HEAVILY DOPED CRYSTALS

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In the present note, we derive an exact formal expression for the self energy of the electronic Green's function for a heavily doped crystal. Several approximations are discussed.

1. Introduction

In recent years, there has been an increased interest in the spectral properties of heavily doped crystals and the electronic structure of alloys [1-8]. In particular, various people have derived approximate formulas for the configuration averaged electronic Green's function for the alloy, notably Soven [4], Matsubara et al. [5], Onodera and Toyozawa [6], and Freed and Cohen [8]. There have also been a number of papers dealing with exact calculations of the disordered lattice [9]. Recently, the theory has been spurred on by the experimental work on amorphous semiconductors.

In the present note, we derive an exact closed expression for the self-energy, $M(z)$, of the configuration averaged electronic Green's function, by using the Zwanzig projection operator technique [10]. This expression, when expanded, gives the Matsubara result term by term and so represents a simple (non-diagrammatic) derivation of this function. We then go on to present a systematic method for approximating the self-energy, which in the first approximation gives an expression very similar to, but not equal to the first approximation of Matsubara (the coherent potential approximation).

2. Derivation of the self-energy

We consider a simple model hamiltonian which represents a heavily isotopically doped crystal [1-3]

$$H = \sum_n \epsilon_n a_n^\dagger a_n + \sum_{n,m} J_{nm} a_n^\dagger a_m, \quad (1)$$

where a_n^\dagger creates an excitation at site n , and ϵ_n is the energy of the molecule at the n th site. For simplicity, we will consider a binary alloy of number fraction X_A of A and X_B of B so that in (1), $\epsilon_n = \pm\Delta$, where we have chosen the zero of energy as the average of the two electronic excited state energies. Since we are considering only singly excited states and the hamiltonian conserves excitation number this is allowable even though the ground state also has zero energy. However, it should be clear that we may also treat the band structure for alloys in the same manner.

We introduce a random variable ξ_n with values ± 1 in the following manner:

$$H = H_0 + V, \quad (2)$$

$$\begin{aligned} H_0 &= \Delta(X_A - X_B) \sum_n a_n^\dagger a_n + \sum_{n,m} J_{nm} a_n^\dagger a_m \\ &= \sum_k \epsilon(k) a_k^\dagger a_k, \end{aligned} \quad (3)$$

$$V = \sum_n \Delta\{\xi_n - (X_A - X_B)\} a_n^\dagger a_n. \quad (4)$$

Thus ξ_n takes the value necessary to make (2) agree with (1). Note that H_0 is now translationally invariant. We define the configuration averaged Green's function and self-energy by

$$G(z) \equiv \langle (z - H)^{-1} \rangle \equiv [z - H_0 - M(z)]^{-1}. \quad (5)$$

It is well known that $G(z)$ is diagonal in k ; that is, the random averaging makes the system translationally invariant. $G(z)$ is the one sided Fourier transform of $\langle \exp(-iHt) \rangle$ and we will find it convenient to deal with this latter form first. Defining a projection operator P by

$$PA = \langle A \rangle, \quad (6)$$

we write

$$g_1(t) = P \exp(-iHt), \quad (7a)$$

$$g_2(t) = (1 - P) \exp(-iHt), \quad (7b)$$

using the equation of motion for $\exp(-iHt)$ and the facts that $g_2(0) = 0$ and $PV = 0$, we find, following Zwanzig,

$$ig_1(t) = PH_0 g_1(t) - i \int_0^t d\tau PV \exp[-i(1-P)H(t-\tau)] V g_1(\tau). \quad (8)$$

Taking the one sided Fourier transform of this equation, we find

$$M(z) = \langle V[z - (1-P)H]^{-1} V \rangle. \quad (9)$$

This is an *exact* result; however it contains the modified hamiltonian $(1-P)H$ and is very difficult to evaluate. This is reminiscent of the usual problem in the evaluation of time correlation functions when the projection operator method is used (e.g., brownian motion). If we expand $[z - (1-P)H]^{-1}$ as

$$[z - (1-P)H]^{-1} = [z - (1-P)H_0]^{-1} + [z - (1-P)H_0]^{-1} (1-P) V [z - (1-P)H]^{-1}, \quad (10)$$

noting that

$$[z - (1-P)H_0]^{-1} = P(z^{-1}) + (1-P)[z - H_0]^{-1},$$

we find that

$$M(z) = \langle V G_0 V \rangle + \langle V G_0 (1-P) V G_0 V \rangle + \langle V G_0 (1-P) V G_0 (1-P) V G_0 V \rangle + \dots, \quad (11)$$

where $G_0 = (z - H_0)^{-1}$. This corresponds to Matsubara's expansion *after* his partial summations leading to the cumulants has been performed. Thus, we have derived, in a simple manner, the result of Matsubara.

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3. Approximation techniques

There is a large "menu" of possible ways of expanding eq. (9) or its Fourier transform and truncating so as to produce suitable approximations. In the following, we give only one such method, which was chosen so as to make contact with Matsubara's first approximation to the self-energy [5]. We introduce this method by defining an operator $F^{(0)}(z)$ by

$$\langle V[z - (1-P)H]^{-1} V \rangle \equiv \langle V[z - (1-P)H_0]^{-1} V \rangle [1 - F^{(0)}(z)]^{-1}, \quad (12)$$

and

$$F^{(0)}(z) = \sum_{n=1}^{\infty} \lambda^n F_n^{(0)}(z). \quad (13)$$

Then by expanding the left hand side and the right hand side we find after performing the necessary averages,

$$F_1^{(0)}(z) = -2\Delta(X_A - X_B) (G_0)_{nn} \sum_k a_k^+ a_k, \quad (14)$$

and the first approximation to $M(z)$ is

$$M^{(0)}(z) = \langle V G_0 V \rangle [1 + 2\Delta(X_A - X_B) (G_0)_{nn}]^{-1}. \quad (15)$$

This corresponds to a summation of the diagrams representing scattering from one site but important multiple occupancy corrections have been omitted [7]. In order to include these in some way, we expand $M(z)$ by defining a new operator $F(z)$

$$\langle V[z - (1-P)H]^{-1} V \rangle \equiv \langle V G V \rangle [1 - F(z)]^{-1}, \quad (16)$$

and

$$F(z) = \sum_{n=1}^{\infty} \lambda^n F_n(z). \quad (17)$$

This gives, in the first approximation,

$$F_1(z) = -2\Delta(X_A - X_B) G_{nn} - (G_{nn})^{-1} (G^2)_{nn} M(z), \quad (18)$$

so that the kk matrix element of M is given by

$$M_{kk}^{(1)}(z) = \frac{4\Delta^2 X_A X_B G_{nn}}{1 + 2\Delta(X_A - X_B)G_{nn} + (G_{nn})^{-1}(G^2)_{nn} M_{kk}^{(1)}(z)}, \quad (19)$$

where

$$(G^2)_{nn} = N^{-1} \sum_k (z - \epsilon_k - M_{kk})^{-2}, \quad (20)$$

and

$$G_{nn} = N^{-1} \sum_k (z - \epsilon_k - M_k)^{-1}. \quad (21)$$

When eq. (19) is compared to the coherent potential approximation (CPA) we find that the difference between them is solely in that the $(G^2)_{nn}$ in (19) is replaced by $(G_{nn})^2$ in the CPA equation [7]. Both eq. (19) and eq. (15) (as well as the CPA) reduce to the exact result in the limit that $J_{nm} = 0$ [where $(G^2)_{nn} = (G_{nn})^2$].

It is easy to carry out higher approximations to $M(z)$ using the definition of $F(z)$ — one must be careful of the non-commutativity of the $F_n(z)$. The use of the $F(z)$ in this way is analogous to a cumulant series in that it sums many diagrams in a geometric manner.

There are a number of interesting questions raised by this method: first, what is the relationship of the approximation of eq. (19) to the CPA, which has been so successful; second, what is the relationship of eq. (19) to the t matrix derivation of Soven;

third, what other possibilities are there for the approximation of M and how do these compare to the CPA. Finally, one may use the present method to calculate higher order Green's functions such as that needed for electron transport [11]. These points will be discussed in a future publication.

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