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PROBLEMS IN STRONG SCATTERING BINARY ALLOYS\*

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ABSTRACT

We present results of model calculations based on two different approximations which were both intended to be improvements over the Coherent Potential Approximation. We show that both approximations yield non-physical solutions; specifically, they predict average Green's functions which contain singularities on both upper and lower half complex energy planes. We conjecture that non-analytic behavior will occur generally in high-order approximations to the average Green's function.

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We report numerical calculations based on two very different extensions of the CPA. One is based on the corrected cumulant scheme of Yonezawa<sup>1</sup> as developed by Nickel and Krumhansl;<sup>2</sup> the other is based on the cluster approach of Butler and Kohn<sup>3</sup> developed to include self-consistency as outlined by Butler.<sup>4</sup> Our calculations of the average Green's function for binary alloys are carried out not only for real energies but for complex energies as well. It is this extension into the complex energy plane that makes these calculations unique and shows absolutely unambiguously that the solutions of the equations for the average Green's function within both approximations contain non-analyticities off the real energy axis. The non-analyticities are branch points in both upper and lower halves of the complex energy plane and are clearly non-physical. We conjecture that these non-analyticities are a general feature of extensions of the CPA. For this reason we suggest that proposed formal approximations be treated with caution until their analytic behavior is understood.

Before we actually describe the numerical calculations we outline what we feel are the most important points to be learned from this calculation. Some of these points may appear trivial -- however we feel that in the past their significance has been overlooked.

1. The exact average Green's function is analytic in the complex energy plane except for a cut along the real axis. That is, because every exact Green's function contributing to the average has singularities only on the real axis one can show that the average and all its derivatives are necessarily bounded off the real axis. Note, however that here and below we confine our discussion to the "physical sheet" defined by the boundary condition  $G(E) \sim E^{-1}$ ,  $E \rightarrow \infty$ , and the reality condition  $G^*(E) = G(E^*)$ . We say nothing about singularities which appear in general on other branches of  $G(E)$ .

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2. Non-analyticity (by which we specifically mean non-analyticity off the real energy axis) makes the approximation unacceptable. Non-analyticity implies such physically nonsensical space and time behavior of the Green's function as solutions growing in time. Also, local properties such as the density of states can no longer be uniquely defined and furthermore sum rules, as for example expressions for the integrated density of states, are no longer satisfied.

3. There is no a-priori reason to expect that an arbitrary approximation to the exact average Green's function will be analytic. Analyticity appears very hard to establish generally; we know of only one approximation scheme for which a general proof has been found.<sup>5</sup>

Note that analyticity has never been proved for the single-site CPA except for certain special models. On the other hand the CPA has been used very extensively and no counter example has ever been found - suggesting that a proof of analyticity might exist. The work of Tsukada<sup>6</sup> and one of us (W. H. Butler, unpublished) is particularly relevant here. These model calculations involve partitioning the system into "molecular" clusters and performing a simple CPA calculation with these clusters as a "single-site" basis.<sup>7</sup> Fairly extensive searches in the parameter space of potential strengths and concentration have not turned up any non-analyticities.

4. The calculations presented here are based on two entirely different formalisms and approximations. Their only points in common are that they are

both attempts to go beyond the CPA to take into account the effects of fluctuations and that they are both self-consistent theories in the sense that the calculated average Green's function is used in the defining equation for the self-energy employed in the calculation. Because of this we feel that analyticity problems in other self-consistent high-order approximations will be the rule rather than the exception. Additional evidence comes from the numerical work of Capek<sup>9</sup> based on yet another approximation scheme.

It is important to realize that the approximations discussed here do yield analytical results for certain choices of the alloy parameters and even when non-analyticity appears, often very reasonable density of states curves can be found. Thus we feel that published results based on other approximate formulations must be treated with caution — one needs to carry out a very extensive search in parameter space to discover whether one's approximation has general validity.

Corrected Cumulant Calculation: We present below a calculation for a one-dimensional tight binding system for a particular set of model parameters. Other calculations, both in one and three dimensions have been performed; the single calculation presented here adequately describes the nature of the problem.

We consider the model Hamiltonian  $H = \sum_{ij} W_{ij} a_j a_i^\dagger + \sum_i \epsilon_i a_i^\dagger a_i$  where  $W_{ij}$  is translationally invariant and defines an unperturbed Green's function  $g_{ij}(E) = (2\pi)^{-1} \int dk \exp(ikR_{ij}) (E - \cos ka)^{-1}$ . Randomness is contained in  $\epsilon_i$  which we take to be  $\epsilon_+ = 1.75$  with probability  $c = .25$  and  $\epsilon_- = 0$  with probability  $1-c = .75$ . Note that the band splitting parameter  $\delta = (\epsilon_+ - \epsilon_-) / (\text{half band width})$  equals 1.75; we are in a strong scattering regime.

We use the corrected cumulant scheme described in Nickel and Krumhansl (NK) and truncate the self-energy at the level of pairs, nearest and next-nearest neighbor only. That is, we take the self-energy to be  $\Sigma(k) = \Sigma_{00}^{(1)} + 2\Sigma_{00}^{(2)}(1) + 2\Sigma_{00}^{(2)}(2) + 2\Sigma_{01}^{(2)} \cos ka + 2\Sigma_{02}^{(2)} \cos 2ka$ . Our approximate average Green's function is then given by  $\langle G \rangle_{ij} = (2\pi)^{-1} \int dk \exp(ikR_{ij}) (E - \cos ka - \Sigma(k))^{-1}$ . To obtain  $\Sigma$  we have to solve equation (22) in NK twice; once to obtain  $\Sigma_{00}^{(1)} + \Sigma_{00}^{(2)}(1)$  and  $\Sigma_{01}^{(2)}$  in terms of  $\langle G \rangle_{00}$  and  $\langle G \rangle_{01}$ , and again to obtain  $\Sigma_{00}^{(1)} + \Sigma_{00}^{(2)}(2)$  and  $\Sigma_{02}^{(2)}$  in terms of  $\langle G \rangle_{00}$  and  $\langle G \rangle_{02}$ . We must also solve the CPA(1) equation to obtain  $\Sigma_{00}^{(1)}$  in terms of  $\langle G \rangle_{00}$ . These equations in addition to the equations for  $\Sigma(k)$  and  $\langle G \rangle_{ij}$  given above then completely define the problem. The numerical work is completely straightforward. We require the three matrix elements  $\langle G \rangle_{00}$ ,  $\langle G \rangle_{01}$ , and  $\langle G \rangle_{02}$  and these we obtain by iteration using a Newton-Raphson technique.

The equations are highly non-linear and yield many solutions. We determine the correct solution by starting at a very large value of the energy where we know the asymptotic values of the quantities appearing in the equations. We then follow this unique solution towards the energy region of interest. The self-energy  $\Sigma_{00}^{(1)}(E)$  obtained in this calculation is shown in Fig. 1 for a small region in the complex energy plane. Because of the existence of branch point singularities off the real axis one is forced to introduce branch cuts to define a single valued function  $\Sigma_{00}^{(1)}(E)$ . This is a largely arbitrary procedure; we have chosen to draw cuts perpendicular to the real axis. Note that  $\langle G(E) \rangle_{00}$  necessarily has the same analytic structure and thus, for example, the density of states ( $\text{Im} \langle G(E) \rangle_{00}$  on the real axis) will show step discontinuities.

We have already outlined why such behavior in  $\Sigma(E)$  and  $\langle G(E) \rangle$  is unsatisfactory. We now discuss to what extent it can be considered a general feature. First, when we truncated the self-energy at nearest neighbor pairs only we could not find any non-analyticities in this one-dimensional model but we did find them in a similar strong scattering high concentration regime in a three dimensional simple cubic model. If we extend the self-energy to include pairs out as far as eighth-nearest neighbor (in one-dimension) the non-analyticities remain. Finally, they also occur if we include nearest and next-nearest neighbor pairs and the close packed triplet configuration in the self-energy. A large range of concentration and scattering strengths has not been investigated;

Self-Consistent Cluster Calculation: The calculation described below was based on the same model Hamiltonian as the corrected cumulant calculation described above. Although the nature and motivation of the approximations are quite different similar off-axis singularities are observed for some concentrations and band splittings.

The scheme used is that of reference 4.<sup>10</sup> The average density of states per site,  $\int \rho(E) dE$ , is calculated for a site at the center of a cluster. The sites within the cluster are treated exactly during the configurational average while those outside the cluster are described by an effective Hamiltonian,

$$H = \sum_{ij} W_{ij} a_j^+ a_i + \sum_i \bar{E} a_i^+ a_i.$$



Self-consistency is introduced by choosing  $\bar{E}$  so that the average density of states per site calculated for the site at the center of the cluster is equal to the density of states calculated for the <sup>(Thus we choose)</sup> medium;  $\sqrt{G_{00}} = \bar{G}_{00}$ . Here  $\bar{G}$  is the Green's function calculated with self-energy  $\bar{E}$  on all sites.

Figure 2(a) shows the diagonal element of the Green's function,  $\bar{G}_{00}$  calculated for a three site cluster with  $\epsilon_+ = 2$  and  $\epsilon_- = 0$ , both with probability .5.  $W$  is taken to be .5 so that the band splitting parameter,  $\delta$ , is 2. Note the branch point occurring for  $\text{Re}E \approx 2.1$ . Figures 2(b) and 2(c) compare the true density of states to that obtained from this approximation. The curve in 2(c) was obtained by drawing the branch cut in  $G$  parallel to the  $\text{Im}E$  axis.

We have investigated several values of  $\delta$  as well as several concentrations and cluster sizes. Off-axis branch points are characteristic of large  $\delta$  and high concentration. They exist for five site clusters as well as for three sites. In the work of reference 4 branch points exist above the real energy axis at many of the peaks in the density of states. Difficulties in following, numerically, the solution to the self-consistent cluster equation through the peaks were not recognized as being due to off-axis branch points. The analyticity problems of the self-consistent cluster approach and possible solutions to these difficulties will be discussed more fully in a subsequent publication.

Brouers et al.<sup>10</sup> have used the method of reference 4 (coupled with a further approximation which simplifies the numerical problems in three dimensions) to calculate the density of states of a model simple cubic disordered alloy. When we repeated their calculation for a somewhat higher value of  $\delta$  ( $\delta = 2$ ) than the one they used we found regions in the complex  $E$  plane in which no solution could be obtained. This is not simply a numerical problem, but is related to the branch points which occur in the one-dimensional calculation. In our opinion the utility of the self-consistent cluster technique in three dimensions is still an open question which we hope to discuss further elsewhere.

Conclusions: We feel that the results described above require a complete reappraisal of all methods based on averaging as used to date to describe excitations in random systems. In the hope of stimulating additional research we conjecture that self-consistency arbitrarily applied or equations of motion arbitrarily truncated will not work because one has not taken into account properly the interactions between different fluctuating components of the field, e.g., pair and triplet resonances in the corrected cumulant scheme, resonances in different spatially localized clusters in the cluster scheme. To be more specific, we note that the pair approximation of NK allows pair fluctuations throughout the crystal and also couples them all by introducing self-energy matrix elements between all possible pairs. The self-consistent cluster approach of Butler allows for fluctuations in only one region of the crystal and not elsewhere by forcing a medium description in terms of a single site-diagonal self-energy. Finally, the CPA of Tsukada again allows for fluctuations in all regions of the crystal but it specifically excludes any interactions by never introducing matrix elements of the self-energy between different "molecules." Thus in some sense this "molecular" CPA appears as the mean; of course, it is not at all obvious that this has anything whatever to do with the fact that it seems to yield analytical results.

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## References

- <sup>1</sup>F. Yonezawa, *Progr. Theoret. Phys. (Kyoto)* 40, 734 (1968).
- <sup>2</sup>B. G. Nickel and J. A. Krumhansl, *Phys. Rev.* B4, 4354 (1971).
- <sup>3</sup>W. H. Butler and W. Kohn, *J. Res. National Bureau of Standards* 74A, 443 (1970).
- <sup>4</sup>W. H. Butler, *Phys. Letters* 39A, 203 (1972).
- <sup>5</sup>R. H. Kraichnan, *J. Math. Phys.* 2, 124 (1961).
- <sup>6</sup>M. Tsukada, *J. Phys. Soc. Japan* 26, 684 (1969).
- <sup>7</sup>This approximation must be considered as a true CPA as compared with, say, the CPA(n) of Nickel and Krumhansl. The crucial distinguishing feature is that in this approximation there are no matrix elements of the self-energy linking different clusters.
- <sup>8</sup>A seven percent error in the total integrated density of states (suggestive of a branch cut) in the work of Tsukada has been checked by us and is apparently due to numerical error.
- <sup>9</sup>V. Capek, *Phys. Status Solidi* 43, 61 (1971) and *Czech. J. Phys.* B21, 997 (1971).
- <sup>10</sup>The same approximation appears to have been suggested independently by F. Brouers, M. Cyrot, and F. Cyrot-Lackman (to be published) and also by V. Capek, *Physica Status Solidi (b)* 52, 399 (1972).

## List of Figures

Fig. 1. Contours of equal real and imaginary parts of the self-energy in the pair approximation of NK. The solution has been chosen such that  $\langle G(E) \rangle \approx E^{-1}$  for large  $E$ .

Fig. 2. (a) Contours of equal real and imaginary parts of the Green function,  $\bar{G}_{00}$ , in the self-consistent cluster approximation. The solution has been chosen such that  $\bar{G}(E) \approx E^{-1}$  for large  $E$ . (b) Exact density of states. (c) Density of states from the self-consistent cluster approximation. The dashed line at  $\text{Re}E \approx 2.1$  indicates where the branch cut has been drawn. The dashed line at  $\text{Re}E \approx 2.3$  is due to an uncertainty in the density of states associated with a singularity on the  $\text{Re}E$  axis. The Green's function is continuous at  $\text{Re}E \approx 2.3$  for  $\text{Im}E$  slightly greater than zero.

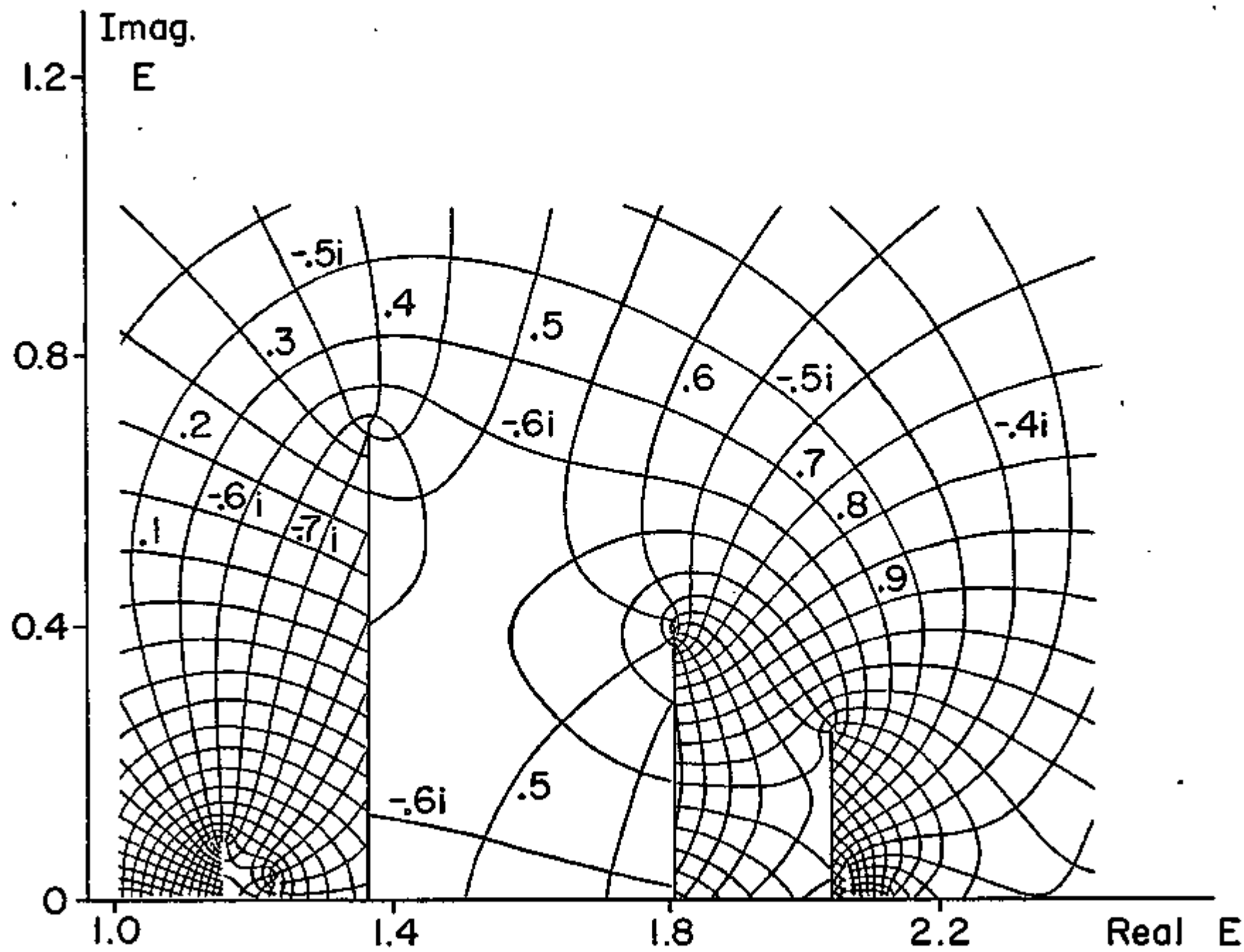


Figure 1

Figure 2

