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New method for self-consistency in disordered systems

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Effective-medium theories for the electronic structure of disordered systems often lead to self-consistent equations for the self-energy. We present a powerful method which solves for the self-energy by converting the integral equations into a system of simultaneous equations. We consider two distinct cases: tight binding and muffin tin. Convergence is easily obtained where previously it was very difficult. Further, we provide a physically appealing and useful interpretation to our method.

One approach to an understanding of disordered systems is to replace the disordered medium by an effective medium. For the case of electrons in a substitutionally disordered medium the coherent-potential approximation[1] (CPA) and some proposed extensions of it[2,3] are used. For the case of positionally disordered (amorphous) systems, the effective-medium approximation (EMA) of Roth[4] is generally regarded to be the best method,[4–7] although it is one of the most difficult computationally. The replacement of the disordered medium by an effective medium often leads to coupled nonlinear and nearly singular integral equations for the self-energy.

We shall present a powerful method to solve for the self-energy. It consists of first converting the integral equations to a large system of simultaneous nonlinear equations. Solving this system yields the single-particle Green's function and related physical quantities such as the density of states (DOS). There exist many methods which may be used to solve this system of equations.[8] In particular, we select the complementary Broyden approach.[8,9] Our method is particularly useful in dealing with problems of positional disorder (the EMA) (Ref. 4) and the extensions of the CPA.[2,3] Further, we provide a physically appealing interpretation to our method. The interpretation is based on the two-particle Green's function. The latter is related in a simple way to transport properties in disordered systems via the Kubo-Greenwood formula.[10,11]

We illustrate our method by considering the EMA (Ref. 4) in detail. We define the tight-binding unaveraged Green's function G_{ij} as[6,12]

$$\sum_l (ES_{il} - H_{il}) G_{lj} = \delta_{ij} \tag{1}$$

Here i, j, and l refer to site indices. H_{ij} and S_{ij} are the transfer and overlap integrals, respectively. The averaged Green's function in momentum space is given by

$$G_{\vec{k}}^{(E)} = \frac{n}{E - nM_{\vec{k}} - \Sigma_d} , \tag{2}$$

where

$$nM_{\vec{k}} = n\tilde{H}_{\vec{k}} + \Sigma_{l\vec{k}} , \tag{3}$$

$$\tilde{H}_{\vec{k}} = \int [H(\vec{r}) - ES(\vec{r})] g(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d\vec{r} . \tag{4}$$

Here n and $g(\vec{r})$ are the number density and pair distribution function (PDF), respectively. The nature of the various proposed approximations is determined by equations describing the self-energy Σ_d and Σ_{lk}. In the EMA of Roth[6]

$$\Sigma_d = \int H_{\vec{k}} G_{\vec{k}} M_{\vec{k}} \frac{d\vec{k}}{8\pi^3} , \tag{5a}$$

$$\Sigma_{l\vec{k}} = n \int h(\vec{k} - \vec{k}') M_{\vec{k}'}^2 G_{\vec{k}'} \frac{d\vec{k}'}{8\pi^3} , \tag{5b}$$

and $h(\vec{r}) = g(\vec{r}) - 1$ is the pair correlation function.

Almost all the proposed effective-medium theories may be cast in the above form with different expressions for the right-hand side (rhs) of Eq. (5). In Eq. (18) we shall give an example of a different approximation. The self-consistency problem is to find $M_{\vec{k}}$ and Σ_d such that Eq. (5) is satisfied. One usually takes $S(r)$ to have an exponential form

$$S(r) = e^{-r/a_0} [1 + r/a_0 + \tfrac{1}{3}(r/a_0)^3] , \tag{6}$$

where a_0 is a parameter which governs the range of $S(r)$. $H(r)$ is proportional to $S(r)$. Details of the model are provided in Ref. 6. For the muffin-tin case treated in this work we have selected a single phase shift which mimics the resonant d phase shift of Ni. The formalism and details have been described before.[13]

To solve Eqs. (3) and (5b) numerically, one assumes that the integrand can be evaluated on a set of mesh points $\{k_i\}$ where we make an implicit assumption that all functions in the integrand are available at every k_i. We have on using Eqs. (3) and (5)

$$M(k_i)=n\widetilde{H}(k_i)+\sum_{l=1}^{N} w_{il}h(k_i,k_l)M^2(k_l)G(k_l)\ , \tag{7a}$$

where

$$h(k_i,k_j)=\int_{|k_i-k_j|}^{|k_i+k_j|} h(s)s\,ds \tag{7b}$$

and w_{il} are the weighting factors for numerical integration. One procedure is simple iteration where one guesses a form for $M_{\vec{k}}$ $(=M_{\vec{k}}^{(0)})$ and iterates the above equation. Note, however, that the iteration procedure is not relevant to the final solution. The $M(k_i)$ are determined from Eq. (7) and it does not matter how one gets to them as long as the final result can be shown to satisfy Eq. (7). This prompts us to regard Eq. (7) as a large system of simultaneous equations, one for each point k_i of interest. Consider the following functional

$$F_{k_i}[\{M_{k_l}\}]=M(k_i)-n\widetilde{H}(k_i)-\sum_{l=1}^{N} w_{il}h(k_i,k_j)M^2(k_l)G(k_l)\ . \tag{8}$$

Note that the coupled Eq. (5a) can be included in Eq. (8) by augmenting the vector function $\underline{F}(\underline{M})$.

One can now use powerful quasi-Newton methods to solve this system.[8] We select the complementary Broyden method which has several advantages: (i) It does not require explicit derivatives (as do the Newton and Gauss-Seidel methods). (ii) It does not require inverting large matrices even for problems with many variables such as ours (one has an N^2 instead of an N^3 process). (iii) The convergence is rapid. This last point is achieved by using the information from the entire past history to guide the present iteration.

The following is a brief description of the complementary Broyden method[8,9] as applied to our problem. Let us consider a Taylor expansion of Eq. (8)

$$\underline{F}(\underline{M})\cong\underline{F}(\underline{M}^{(p)})+\underline{J}(\underline{M}-\underline{M}^{(p)})\ . \tag{9}$$

Here p denotes the iteration number and the Jacobian matrix of first partial derivatives has the following elements:

$$\underline{J}_{ij}=\delta_{ij}-w_{ij}h(k_i,k_j)\times[2M(k_j)G(k_j)+M^2(k_j)G^2(k_j)]\ . \tag{10}$$

Newton's method which forms the basis of most modern methods, specifies that the "guess" $\underline{M}^{(p+1)}$ for the next iteration be one that makes the rhs of Eq. (9) vanish, i.e.,

$$\underline{M}^{(p+1)}=\underline{M}^{(p)}-[\underline{J}]^{-1}\cdot\underline{F}[\underline{M}^{(p)}]\ .$$

Since the matrix $\underline{J}^{-1}$ is generally not available, we approximate it based on information from previous iterations, i.e.,

$$\underline{M}^{(p-1)}=\underline{M}^{(p)}+[\underline{J}^{-1}]^{(p)}\times[\underline{F}(\underline{M}^{(p-1)})-\underline{F}(\underline{M}^{(p)})]\ . \tag{11}$$

Thus Eq. (9) is used on the previous step to define $[\underline{J}^{-1}]^{(p)}$. However, Eq. (11) places only N constraints on the N^2 elements of $\underline{J}^{-1}$. To completely specify $[\underline{J}^{-1}]^{(p)}$ and further, to retain information of the iteration history, we demand that the Frobenius norm of the change be minimized,

$$\delta\sum_{ij}[(\underline{J}^{-1})_{ij}^{(p)}-(\underline{J}^{-1})_{ij}^{(p-1)}]^2=0 \tag{12}$$

We then use the method of Lagrange multipliers to include the constraint Eq. (11) and obtain

$$(\underline{J}^{-1})^{(p)}=(\underline{J}^{-1})^{(p-1)}+\frac{\{\underline{\Delta M}^{(p-1)}-(\underline{J}^{-1})^{(p-1)}\underline{\Delta F}^{(p-1)}\}(\underline{\Delta F}^{T})^{(p-1)}}{|\underline{\Delta F}^{(p-1)}|^2}\ , \tag{13}$$

where

$$\underline{\Delta M}^{(p-1)}=\underline{M}^{(p)}-\underline{M}^{(p-1)}\ ,$$

$$\underline{\Delta F}^{(p-1)}=\underline{F}^{(p)}-\underline{F}^{(p-1)}\ .$$

An initial guess for the Jacobian inverse is needed. If we choose to model the initial guess by a diagonal constant matrix[14]

$$(\underline{J}^{-1})^{(1)}=\alpha\underline{I}\ , \tag{14}$$

where α is between zero and unity, we obtain from Eq. (9),

$$M_{\vec{k}}^{(2)}=(1-\alpha)M_{\vec{k}}^{(1)}+\alpha\left[\widetilde{H}_{\vec{k}}+\int h(\vec{k}-\vec{k}\,')(M_{\vec{k}'}^{(0)})^2G_{\vec{k}'}^{(0)}\frac{d\vec{k}\,'}{8\pi^3}\right]\ . \tag{15}$$

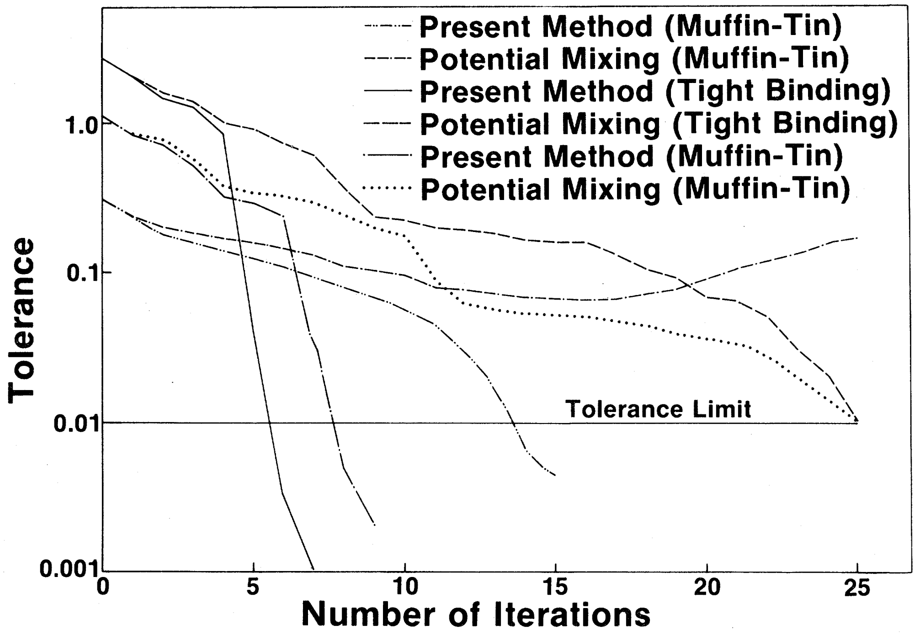

FIG. 1. Comparison of convergence rates. For the tight-binding case we picked a point at $E=4.0$ (see Fig. 2 below). For the muffin-tin case we chose $E=0.6125$ and 0.56 Ry (see Fig. 3 below). The $E=0.56$ Ry case diverges if merely potential mixing is used (see also Ref. 15). Note that the y axis is a log scale.

This is "potential mixing" (also called simple iteration when $\alpha=1$).

Figure 1 compares the convergence rates of the proposed method with potential mixing, for typical cases. For some choices of the energy, the potential mixing actually diverges.[15,16] The convergence rate of our method is dramatically better.

In Fig. 2 we plot the DOS for the tight-binding model. The shaded areas are regions where convergence in the EMA was not obtained even with *60* iterations either by potential mixing or Pratt scheme. Our method converges within *15* iterations even for these difficult regimes. We note the following: (i) The EMA agrees well with calculations done via the negative eigenvalue method, by Fujiwara and Tanabe.[17] (ii) The present method shows that the EMA yields the band edge at $E \simeq 8.2$ in agreement with the Fujiwara-Tanabe calculations and in remarkable contrast to other effective medium theories which do poorly at the band edges. (iii) The EMA is observed to behave analytically for all energies. We have also plotted the DOS for a recently

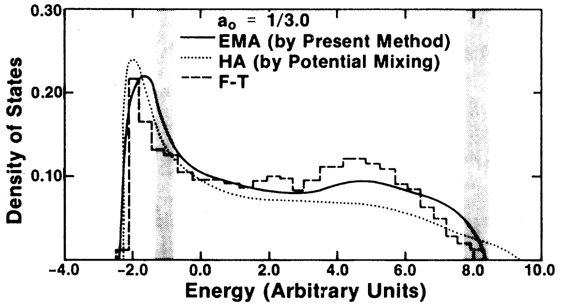

FIG. 2. Density of states for the nonorthogonal tight-binding model. The shaded areas represent regions where the EMA failed to converge by conventional methods. See text for a discussion.

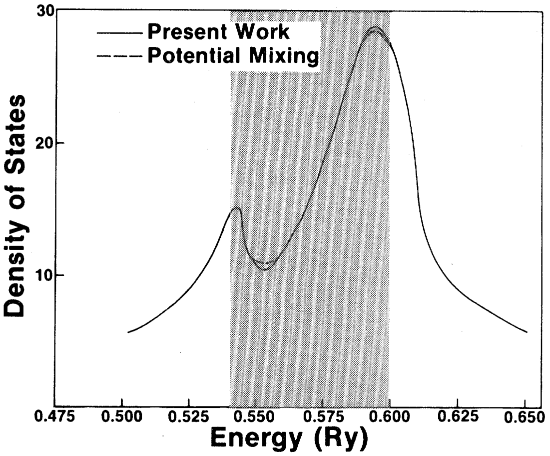

FIG. 3. Density of states for a single phase-shift model of liquid Ni. The shaded area represents a region where convergence by conventional methods is very difficult to obtain (see Ref. 15). The small differences in the two curves is because higher accuracy is possible by the rapidly converging proposed method.

proposed herglotz approximation (HA)[18] where convergence was obtained by potential mixing. The reason for the success of the potential mixing method in this case is discussed below [Eq. (18)]. Other herglotz approximations[19,20] do worse than the one plotted here. Figure 3 shows the DOS for a single phase-shift muffin-tin model of liquid Ni.

The experience with the calculations in Figs. 2 and 3 suggests that on an average, EMA calculations can be done with *greater accuracy* and an *order-of-magnitude reduction in computer time* by the proposed method. This could be very useful in treating sophisticated models of nonsimple liquid metals,[21] complex alloy systems such as metallic glasses and extensions of effective medium theories to problems in elasticity[22] and electromagnetic scattering.

The proposed method will also be very useful for many problems in substitutionally disordered systems. Some examples are the following: (i) for a multiband (eight or more bands) case where one has both diagonal and off-diagonal disorder[23] (an example is the important semiconducting quarternary alloy $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}_y\mathrm{P}_{1-y}$), (ii) cluster CPA calculations where the complexity of the problem goes as the square of the cluster size,[3] (iii) recently proposed extensions of the CPA where the self-energy is $\vec{\mathrm{k}}$ dependent,[2] and (iv) substitutionally disordered Heisenberg ferromagnets and antiferromagnets.[24]

We offer a physically appealing interpretation to the inverse of the Jacobian. The conductivity tensor for a system with short-range order has recently been derived.[11,25] For a tight-binding model in the EMA one has[11]

$$\underline{\sigma}(E)=\frac{1}{\pi}\int \vec{\mathrm{j}}^{\,0}_{\vec{\mathrm{k}}}\,\vec{\mathrm{j}}_{\vec{\mathrm{k}}}\{\mathrm{Re}[G^2_{\vec{\mathrm{k}}}\lambda_{\vec{\mathrm{k}}}(E,E)] + |G_{\vec{\mathrm{k}}}|^2\lambda_{\vec{\mathrm{k}}}(E,E')\}\frac{d\vec{\mathrm{k}}}{8\pi^3}\;. \tag{16}$$

Here the *j*'s are the current matrix elements. $\lambda_{\vec{\mathrm{k}}}(E,E')$ are related to the vertex corrections with

$$[E,E'\rightarrow(E+i\eta,E-i\eta)]$$

understood. In Ref. 11 an approximation to $\lambda_{\vec{\mathrm{k}}}$ was defined, which was called the Rubio-Ashcroft-Schaich approximation.[26] Within such an approximation, one can show

$$\vec{\lambda}(E,E)=(\underline{J})^{-1}\underline{I}\;, \tag{17}$$

where $\underline{I}$ is a vector with each element equal to unity. The Jacobian needed to obtain the single-particle Green's function can similarly be related to the two-magnon response function for disordered ferromagnets and the lattice thermal conductivity for the phonon case.

We have treated the EMA in detail. For a number of theories which rigorously satisfy analyticity requirements (e.g., herglotz theories)[18–20] one can obtain simple forms for the Jacobian. For the Gyorffy-Korringa-Mills theory,[19] Eqs. (5) become, for example,

$$\Sigma_d+n^M_{\vec{\mathrm{k}}}=n\vec{\mathrm{H}}_{\vec{\mathrm{k}}}+\int[1+nh(\vec{\mathrm{k}}-\vec{\mathrm{k}}')]H^2_{\vec{\mathrm{k}}'}G_{\vec{\mathrm{k}}'}\frac{d\vec{\mathrm{k}}'}{8\pi^3}\,. \tag{18}$$

Using the fact that $1+nh(\vec{\mathrm{k}}=0)=0$ and if $H_{\vec{\mathrm{k}}}$ is a rapidly decaying function, one can show that for these theories the Jacobian is approximately an identity matrix. Recall Eqs. (14) and (15), and one sees why a simple iterative scheme will be successful for these theories. This is indeed why in Fig. 2, the HA (Ref. 18) converges easily by potential mixing. Further, we have on using Eq. (17) that the vertex corrections may be small for these theories. A similar method has been used successfully for the band structure of ordered, but complex semiconductors.[27]

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[14] One need not always make such a simplified choice of the inverse Jacobian. For example in Fig. 2, to obtain

convergence at $E=3.5$, one could choose the inverse Jacobian from the converged result at $E=3.0$ as an initial guess.

[15] In Ref. 13, convergence was obtained for this case by taking the Percus-Yerick hard-core diameter $\sigma=5.0$ a.u. and decreasing it stepwise to the value of liquid Ni ($\sigma=4.188$ a.u.). In each step potential mixing is done. In the final stage one switches from the Percus-Yerick PDF to the experimental PDF of liquid Ni. This is a sucessful, but lengthy procedure.

[16] The Newton method has quadratic convergence, and the complementary Broyden has superlinear convergence rates. Potential mixing (and Pratt) have poorer linear convergence rates.

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