Alternative self-energy expression for the Anderson model

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A closed system of equations for the Green's functions is found by applying the functional-derivative technique at the third level in the coupled chain of equations. From this set of equations an exact expression for the impurity atom's self-energy is obtained which involves only first-order functional derivatives. A procedure is proposed for generating nonperturbative solutions to arbitrary accuracy in a systematic manner. As an illustration, a solution is presented in which the functional derivatives are evaluated using the Hartree-Fock approximation. The spectral density function is calculated for the symmetric case and is found to have the correct behavior for all values of U/Δ.

I. INTRODUCTION

Since its introduction, the Anderson model[1] has been the subject of a considerable amount of theoretical analysis. Besides a continued importance in magnetic impurity problems,[2] the model has a significant role in mixed valence theory[3] and in chemisorption theory.[4] Solutions found in one context are generally not applicable in another. For example, in the magnetic impurity problems it is meaningful to consider the cases where the Coulomb repulsion U is infinite[5] or the mixing parameter is small.[6] For problems in chemisorption theory, it is usually necessary to obtain solutions which are valid for arbitrary values of these parameters.

In this paper, a new exact expression for the impurity atom's self-energy is found using the functional-derivative technique.[7] The Hamiltonian having the form

$$H=\sum_{k,\sigma}E_{k\sigma}c^{\dagger}_{k\sigma}c_{k\sigma}+\sum_{\sigma}(E_{d\sigma}c^{\dagger}_{d\sigma}c_{d\sigma}+\tfrac{1}{2}Uc^{\dagger}_{d\sigma}c_{d\sigma}c^{\dagger}_{d\bar{\sigma}}c_{d\bar{\sigma}}) +\sum_{k,\sigma}(V_{dk}c^{\dagger}_{d\sigma}c_{k\sigma}+V_{kd}c^{\dagger}_{k\sigma}c_{d\sigma}) \tag{1}$$

is considered, where the operator $c^{\dagger}_{k\sigma}$ ($c_{k\sigma}$) creates (destroys) electrons in the metal states with energy $E_{k\sigma}$ and the operator $c^{\dagger}_{d\sigma}$ ($c_{d\sigma}$) creates (destroys) electrons on the impurity atom with energy $E_{d\sigma}$ or $E_{d\sigma}+U$. The electron spin is denoted by σ ($\bar{\sigma}=-\sigma$). No assumptions are made regarding the parameters of this Hamiltonian.

In the next section a brief review of the functional-derivative technique is given. The treatment is slightly different from that given in Ref. 7. The Hamiltonian

$$H=\sum_{\nu}\epsilon_{\nu}c^{\dagger}_{\nu}c_{\nu}+\tfrac{1}{2}\sum_{\nu_1,\nu_2,\nu_3,\nu_4}V'_{\nu_1\nu_2\nu_3\nu_4}c^{\dagger}_{\nu_1}c^{\dagger}_{\nu_2}c_{\nu_3}c_{\nu_4}\ , \tag{2}$$

is considered, where $V'_{\nu_1\nu_2\nu_3\nu_4}$ is a matrix element of the two-particle interaction V' and satisfies

$$V'_{\nu_1\nu_2\nu_3\nu_4}=V'_{\nu_2\nu_1\nu_4\nu_3}\ . \tag{3}$$

Some other general relationships are given which will be useful in the following sections.

In Sec. III the functional-derivative technique is applied to the Hamiltonian of Eq. (1). Two expressions for the impurity atom's self-energy are derived from the Green's-function equations of motion. In the first instance the self-energy is shown to yield an expansion in U and $G_{dd\sigma}$, the impurity atom's Green's function. In the second instance a more complex expansion is found. It is suggested that the iterative solutions of the first expression may be used to evaluate the functional derivatives of the second expression. In this way, in principle, nonperturbative solutions of arbitrary accuracy may be generated for the Anderson model.

In Sec. IV the simplest solution of the first expression (the Hartree-Fock approximation) is used to evaluate the functional derivatives in the alternative expression. The resulting solution is used to calculate the spectral density function for the symmetric case. In Sec. V, a discussion is given of the relationship of the self-energy to decoupling approximations.

II. FUNCTIONAL-DERIVATIVE TECHNIQUE

According to Kadanoff and Baym,[7] the single-particle Green's function is defined as

$$G_{\nu\nu'}(tt')=\frac{1}{i}\frac{\langle T[\hat{S}c_{\nu}(t)c^{\dagger}_{\nu'}(t')]\rangle}{\langle T[\hat{S}]\rangle} \equiv\langle\langle c_{\nu}(t);c^{\dagger}_{\nu'}(t')\rangle\rangle\ , \tag{4}$$

where T is the time ordering operator, $\langle\ \rangle$ denotes the grand canonical average, and the operator $\hat{S}$ is given by

$$\hat{S}=\exp\left[-i\int_0^{-i\beta}\sum_{\nu,\nu'}\hat{U}_{\nu\nu'}(t)c^{\dagger}_{\nu}(t)c_{\nu'}(t)\right]\ . \tag{5}$$

The operator $\hat{U}$ corresponds to an arbitrary auxiliary field and β is the inverse temperature.

The equation of motion for the single-particle Green's function is

$$\left[i\frac{\partial}{\partial t}-\epsilon_\nu\right]G_{\nu\nu'}(tt')=\delta_{\nu\nu'}\delta_{tt'}+\sum_{\nu_1}\hat{U}_{\nu\nu_1}(t)G_{\nu_1\nu'}(tt')+\sum_{\nu_1,\nu_2,\nu_3}V'_{\nu\nu_1\nu_2\nu_3}\Gamma_{\nu_1\nu_2\nu_3\nu'}(tt')\ , \tag{6}$$

where the two-particle Green's function $\Gamma_{\nu_1\nu_2\nu\nu'}(tt')$ is given by

$$\Gamma_{\nu_1\nu_2\nu\nu'}(tt')=\frac{1}{i}\frac{\langle T[\hat{S}c_\nu(t)c^\dagger_{\nu_1}(t)c_{\nu_2}(t)c^\dagger_{\nu'}(t')]\rangle}{\langle T[\hat{S}]\rangle}\equiv\langle\langle c_\nu(t)c^\dagger_{\nu_1}(t)c_{\nu_2}(t);c^\dagger_{\nu'}(t')\rangle\rangle\ . \tag{7}$$

The two-particle Green's function is generated by taking the functional derivative of the single-particle Green's function

$$\Gamma_{\nu_1\nu_2\nu\nu'}(tt')=\left[i\frac{\delta}{\delta\hat{U}_{\nu_1\nu_2}(t)}+\langle c^\dagger_{\nu_1}(t)c_{\nu_2}(t)\rangle_{\hat{U}}\right]G_{\nu_1\nu'}(tt')\ , \tag{8}$$

where

$$\langle\cdots\rangle_{\hat{U}}\equiv\frac{\langle T[\hat{S}\cdots]\rangle}{\langle T[\hat{S}]\rangle}\ . \tag{9}$$

Equation (6) may be put into matrix form

$$LG-\Theta G=I\ , \tag{10}$$

where

$$L_{\nu\nu'}(tt')=\left[\left[i\frac{\partial}{\partial t}-\epsilon_\nu\right]\delta_{\nu\nu'}-\hat{U}_{\nu\nu'}(t)\right]\delta_{tt'}\ , \tag{11}$$

$$\Theta_{\nu\nu'}(tt')=\sum_{\nu_1,\nu_2}V'_{\nu\nu_1\nu_2\nu'}\times\left[i\frac{\delta}{\delta\hat{U}_{\nu_1\nu_2}(t)}+\langle c^\dagger_{\nu_1}(t)c_{\nu_2}(t)\rangle_{\hat{U}}\right]\delta_{tt'} \tag{12}$$

and I is the unit matrix. Defining the self-energy Σ by

$$G^{-1}=G_0^{-1}-\Sigma\ , \tag{13}$$

one finds

$$\Sigma=\Theta G\cdot G^{-1}\ , \tag{14}$$

where

$$G_0^{-1}=L\ . \tag{15}$$

The matrix elements of Σ are

$$\begin{aligned}\Sigma_{\nu\nu'}(tt')&=\int_0^{-i\beta}dt_1dt_2\sum_{\nu_1,\nu_2}\Theta_{\nu\nu_2}(tt_1)G_{\nu_1\nu_2}(t_1t_2)G^{-1}_{\nu_2\nu'}(t_2t')\\&=\int_0^{-i\beta}dt_1\sum_{\nu_1,\nu_2,\nu_3,\nu_4}V'_{\nu\nu_1\nu_2\nu_3}\left[i\frac{\delta}{\delta\hat{U}_{\nu_1\nu_2}(t)}+\langle c^\dagger_{\nu_1}(t)c_{\nu_2}(t)\rangle_{\hat{U}}\right]G_{\nu_3\nu_4}(tt_1)G^{-1}_{\nu_4\nu'}(t_1t')\\&=\sum_{\nu_1,\nu_2}V'_{\nu\nu_1\nu_2\nu'}\langle c^\dagger_{\nu_1}(t)c_{\nu_2}(t)\rangle_{\hat{U}}\delta_{tt'}+\Sigma^c_{\nu\nu'}(tt')\ ,\end{aligned} \tag{16}$$

where

$$\begin{aligned}\Sigma^c_{\nu\nu'}(tt')&=\int_0^{-i\beta}dt_1\sum_{\nu_1,\nu_2,\nu_3,\nu_4}V'_{\nu\nu_1\nu_2\nu_3}i\frac{\delta}{\delta\hat{U}_{\nu_1\nu_2}(t)}G_{\nu_3\nu_4}(tt_1)G^{-1}_{\nu_4\nu'}(t_1t')\\&=-\int_0^{-i\beta}dt_1\sum_{\nu_1,\nu_2,\nu_3,\nu_4}V'_{\nu\nu_1\nu_2\nu_3}G_{\nu_3\nu_4}(tt_1)i\frac{\delta}{\delta U_{\nu_1\nu_2}(t)}G^{-1}_{\nu_4\nu'}(t_1t')\ .\end{aligned} \tag{17}$$

The iterative calculation of the correction Σ^c gives the complete expansion in V' and G.[7] The first-order approximation corresponds to the familiar Hartree-Fock approximation

$$\begin{aligned}\Sigma^{\rm HF}_{\nu\nu'}(tt')&=\sum_{\nu_1,\nu_2}V'_{\nu\nu_1\nu_2\nu'}\langle c^\dagger_{\nu_1}(t)c_{\nu_2}(t)\rangle_{\hat{U}}\delta_{tt'}\\&\quad+\sum_{\nu_1,\nu_2}V_{\nu\nu_1\nu'\nu_2}iG_{\nu_2\nu'}(tt')\delta_{tt'}\ .\end{aligned} \tag{18}$$

III. APPLICATION TO THE ANDERSON MODEL

If one takes the operator $\hat{S}$ to be

$$\begin{aligned}\hat{S}=\exp\Bigg[-i\int_0^{-i\beta}dt\sum_\sigma\{&\hat{E}_{d\sigma}(t)c^\dagger_{d\sigma}(t)c_{d\sigma}(t)\\&+\hat{V}_\sigma(t)c^\dagger_{d\sigma}(t)B_\sigma(t)\\&+[\hat{V}_\sigma(t)]^*B^\dagger_\sigma(t)c_{d\sigma}(t)\}\Bigg]\ ,\end{aligned} \tag{19a}$$

where

$$B_\sigma=\frac{1}{\bar{V}}\sum_k V_{dk}c_{d\sigma},\quad \bar{V}=\left[\sum_k |V_{dk}|^2\right]^{1/2} \tag{19b}$$

and $\hat{E}_{d\sigma}$ and $\hat{V}_\sigma$ are the matrix elements of $\hat{U}$ defined in Sec. II, the equations of motion for Eq. (1) are

$$\left[i\frac{\partial}{\partial t}-E_{d\sigma}(t)\right]G_{dd\sigma}(tt')=\delta_{tt'}+\sum_k V_{dk\sigma}(t)G_{kd\sigma}(tt')+U\Gamma_{d\sigma}(tt')\ , \tag{20a}$$

$$\left[i\frac{\partial}{\partial t}-E_{k\sigma}\right]G_{kd\sigma}(tt')=V_{kd\sigma}(t)G_{dd\sigma}(tt')\ , \tag{20b}$$

$$\left[i\frac{\partial}{\partial t'}-E_{k'\sigma}\right]G_{dk'\sigma}(tt')=G_{dd\sigma}(tt')V_{dk'\sigma}(t')\ , \tag{20c}$$

$$\left[i\frac{\partial}{\partial t}-E_{k\sigma}\right]G_{kk'\sigma}(tt')=\delta_{kk'}\delta_{tt'}+V_{kd\sigma}(t)G_{dk\sigma}(tt')\ , \tag{20d}$$

where

$$E_{d\sigma}(t)=E_{d\sigma}+\hat{E}_{d\sigma}(t),\quad V_{dk\sigma}(t)=V_{dk}[1+\hat{V}_\sigma(t)/\bar{V}]\ ,$$

and

$$\Gamma_{d\sigma}(tt')=\langle\langle c_{d\sigma}(t)n_{d\bar{\sigma}}(t);c_{d\sigma}^\dagger(t')\rangle\rangle=\left[i\frac{\delta}{\delta E_{d\bar{\sigma}}(t)}+\langle n_{d\bar{\sigma}}(t)\rangle_{\hat{U}}\right]G_{dd\sigma}(tt')\ , \tag{21}$$

with $n_{d\bar{\sigma}}=c_{d\bar{\sigma}}^\dagger c_{d\bar{\sigma}}$. Combining Eqs. (20a) and (20b) gives

$$\int_0^{-i\beta}d\tau\,G_{dd\sigma}^0(t\tau)^{-1}G_{dd\sigma}(\tau t')=\delta_{tt'}+U\Gamma_{d\sigma}(tt')\ , \tag{22}$$

where

$$G_{dd\sigma}^0(tt')^{-1}=\left[i\frac{\partial}{\partial t}-E_{d\sigma}(t)\right]\delta_{tt'}-S_\sigma(tt')\ ,$$

$$S_\sigma(tt')=\sum_k V_{dk\sigma}(t)G_{k\sigma}^0(tt')V_{kd\sigma}(t')\ ,$$

and $G_{k\sigma}^0(tt')$ is the inverse of $[i(\partial/\partial t)-E_{k\sigma}]\delta_{tt'}$.

Note that all of the Green's-function elements are simply related to $G_{dd\sigma}$. Thus, one needs only to solve for this component. This is facilitated by defining its inverse by

$$\int_0^{-i\beta}d\tau\,G_{dd\sigma}(t\tau)G_{dd\sigma}(\tau t')^{-1}=\delta_{tt'}\ , \tag{23}$$

and the self-energy by

$$G_{dd\sigma}(tt')^{-1}=G_{dd\sigma}^0(tt')^{-1}-\Sigma_{dd\sigma}(tt')\ . \tag{24}$$

Using Eqs. (21)—(24) to solve for the self-energy gives

$$\Sigma_{dd\sigma}(tt')=U\int d\tau\,\Gamma_{d\sigma}(t\tau)G_{dd\sigma}(\tau t')^{-1}=U\langle n_{d\bar{\sigma}}(t)\rangle\delta_{tt'}+\Sigma_{dd\sigma}^c(tt')\ , \tag{25}$$

where

$$\Sigma_{dd\sigma}^c(tt')=-\int d\tau\,G_{dd\sigma}(t\tau)i\frac{\delta}{\delta E_{d\bar{\sigma}}(t)}G_{dd\sigma}(\tau t')^{-1}\ . \tag{26}$$

Neglecting $\Sigma_{dd\sigma}^c$ gives the well-known Hartree-Fock approximation for the Anderson model:

$$\Sigma_{dd\sigma}^{\rm HF}(tt')=U\langle n_{d\bar{\sigma}}(t)\rangle\delta_{tt'}\ . \tag{27}$$

The first correction is

$$\Sigma_{dd\sigma}^c(tt')=U^2G_{dd\sigma}(tt')G_{dd\bar{\sigma}}(t't)G_{dd\bar{\sigma}}(tt')\ . \tag{28}$$

Thus, calculating $\Sigma_{dd\sigma}^c$ iteratively gives the complete expansion in $G_{dd\sigma}$ and U that one would obtain from the diagrammatic technique. The correction given by Eq. (28) has been used by Schönhammer[8] to calculate the photoemission spectra of hydrogen on nickel. An iterative calculation to fourth order corresponds to the calculation done by Yamada.[9]

From the equation of motion for $\Gamma_{d\sigma}(tt')$ an alternative expression for $\Sigma_{dd\sigma}$ may be derived (dropping the subscript $\hat{U}$):

$$\left[i\frac{\partial}{\partial t}-E_{d\sigma}-U\right]\Gamma_{d\sigma}(tt')=\langle n_{d\bar{\sigma}}(t)\rangle\delta_{tt'}+\sum_k V_{dk\sigma}(t)\Gamma_{k\sigma}(tt')+V_{\bar{\sigma}}(t)\langle\langle c_{d\sigma}(t)c_{d\bar{\sigma}}^\dagger(t)B_{\bar{\sigma}}(t);c_{d\bar{\sigma}}^\dagger(t')\rangle\rangle-V_{\bar{\sigma}}(t)^*\langle\langle c_{d\sigma}(t)B_{\bar{\sigma}}^\dagger(t)c_{d\bar{\sigma}}(t);c_{d\sigma}^\dagger(t')\rangle\rangle\ , \tag{29}$$

where $V_\sigma(t)=\bar{V}+\hat{V}_\sigma(t)$ and

$$\Gamma_{k\sigma}(tt')=\langle\langle c_{k\sigma}n_{d\bar{\sigma}};c_{d\sigma}^\dagger\rangle\rangle\ .$$

The equation of motion for $\Gamma_{k\sigma}(tt')$ is

$$\left[i\frac{\partial}{\partial t}-E_{k\sigma}\right]\Gamma_{k\sigma}(tt')=V_{kd\sigma}(t)\Gamma_{d\sigma}(tt')+V_{\bar{\sigma}}(t)\langle\langle c_{k\sigma}(t)c_{d\bar{\sigma}}^\dagger(t)B_{\bar{\sigma}}(t);c_{d\sigma}^\dagger(t')\rangle\rangle-V_{\bar{\sigma}}(t)^*\langle\langle c_{k\sigma}(t)B_{\bar{\sigma}}^\dagger(t)c_{d\bar{\sigma}}(t);c_{d\sigma}^\dagger(t')\rangle\rangle\ . \tag{30}$$

The Green's functions $\langle\langle c_{m\sigma}c_{d\bar{\sigma}}^\dagger B_{\bar{\sigma}};c_{d\sigma}^\dagger\rangle\rangle$ and $\langle\langle c_{m\sigma}B_{\bar{\sigma}}^\dagger;c_{d\bar{\sigma}}\rangle\rangle$ may be replaced by ($m=d,k$)

$$\langle\langle c_{m\sigma}(t)c^{\dagger}_{d\bar{\sigma}}(t)B_{\bar{\sigma}}(t);c^{\dagger}_{d\sigma}(t')\rangle\rangle=\Delta(\bar{\sigma}t)G_{md\sigma}(tt') , \tag{31a}$$

$$\langle\langle c_{m\sigma}(t)B^{\dagger}_{\bar{\sigma}}(t)c_{d\bar{\sigma}}(t);c^{\dagger}_{d\sigma}(t')\rangle\rangle=[\Delta(\bar{\sigma}t)]^{*}G_{md\sigma}(tt') , \tag{31b}$$

$$\Delta(\bar{\sigma}t)=i\frac{\delta}{\delta V_{\bar{\sigma}}(t)}+\langle c^{\dagger}_{d\bar{\sigma}}(t)B_{\bar{\sigma}}(t)\rangle , \tag{31c}$$

$$\Delta(\bar{\sigma}t)^{*}=i\frac{\delta}{\delta[V_{\bar{\sigma}}(t)]^{*}}+\langle B^{\dagger}_{\bar{\sigma}}(t)c_{d\bar{\sigma}}(t)\rangle . \tag{31d}$$

These relations allow the equation for $\Gamma_{d\sigma}$ to be written as

$$\int_0^{-i\beta}d\tau L_{\sigma}(t\tau)\Gamma_{d\sigma}(\tau t')=\langle n_{d\bar{\sigma}}(t)\rangle\delta_{tt'}+\theta(\bar{\sigma}t)G_{dd\sigma}(tt')+\sum_k V_{dk\sigma}(t)\int_0^{-i\beta}d\tau G^0_{k\sigma}(t\tau)\theta(\bar{\sigma}\tau)G_{kd\sigma}(\tau t') , \tag{32}$$

where

$$\begin{aligned}L_{\sigma}(tt')&=\left[i\frac{\partial}{\partial t}-E_{d\sigma}(t)-U\right]\delta_{tt'}-S_{\sigma}(tt') ,\\ \theta(\bar{\sigma}t)&=V_{\bar{\sigma}}(t)\Delta(\bar{\sigma}t)-[V_{\bar{\sigma}}(t)]^{*}[\Delta(\bar{\sigma}t)]^{*} .\end{aligned} \tag{33}$$

Note that the equations of motion for $G_{dd\sigma}$, $G_{kd\sigma}$, $\Gamma_{d\sigma}$, and $\Gamma_{k\sigma}$ now form a closed system of equations. These are solved for $\Gamma_{d\sigma}$ to give

$$\begin{aligned}\Gamma_{d\sigma}(tt')=&\langle n_{d\bar{\sigma}}(t)\rangle G_{dd\sigma}(tt')+\int_0^{-i\beta}d\tau\lambda_{\sigma}(t\tau)\{U\langle n_{d\bar{\sigma}}(\tau)\rangle[1-\langle n_{d\bar{\sigma}}(\tau)\rangle]+\Omega(\bar{\sigma}\tau)\}G_{dd\sigma}(\tau t')\\&+\int_0^{-i\beta}d\tau\lambda_{\sigma}(t\tau)\Lambda(\bar{\sigma}\tau)G_{dd\sigma}(\tau t')+\int_0^{-i\beta}d\tau d\tau'\lambda_{\sigma}(t\tau')R_{\sigma}(\tau'\tau)G_{dd\sigma}(\tau t')\\&+\int_0^{-i\beta}d\tau d\tau'\lambda_{\sigma}(t\tau')T_{\sigma}(\tau'\tau)G_{dd\sigma}(\tau t') ,\end{aligned} \tag{34}$$

where $\lambda_{\sigma}(tt')$ is the inverse of

$$\left[i\frac{\partial}{\partial t}-E_{d\sigma}-U[1-\langle n_{d\sigma}(t)\rangle]\right]\delta_{tt'}-S_{\sigma}(tt') ,$$

$$\Omega(\bar{\sigma}t)=V_{\bar{\sigma}}(t)\langle c^{\dagger}_{d\bar{\sigma}}(t)B_{\bar{\sigma}}(t)\rangle-V_{\bar{\sigma}}(t)^{*}\langle B^{\dagger}_{\bar{\sigma}}(t)c_{d\bar{\sigma}}(t)\rangle , \tag{35a}$$

$$R_{\sigma}(tt')=\sum_k V_{dk\sigma}(t)\int_0^{-i\beta}d\tau G^0_{k\sigma}(t\tau)\Omega(\bar{\sigma}\tau)G^0_{k\sigma}(\tau t')V_{kd\sigma}(t') , \tag{35b}$$

$$T_{\sigma}(tt')=\sum_k V_{dk\sigma}(t)\int_0^{-i\beta}d\tau G^0_{k\sigma}(t\tau)\Lambda(\bar{\sigma}\tau)G^0_{k\sigma}(\tau t')V_{kd\sigma}(t') , \tag{35c}$$

$$\Lambda(\bar{\sigma}t)=V_{\bar{\sigma}}(t)i\frac{\delta}{\delta V_{\bar{\sigma}}(t)}-[V_{\bar{\sigma}}(t)]^{*}i\frac{\delta}{\delta[V_{\bar{\sigma}}(t)]^{*}} . \tag{35d}$$

Inserting this new expression for $\Gamma_{d\sigma}$ into Eq. (25) gives

$$\Sigma_{dd\sigma}(tt')=U\langle n_{d\bar{\sigma}}(t)\rangle\delta_{tt'}+U^2\lambda_{\sigma}(tt')\{\langle n_{d\bar{\sigma}}(t)\rangle[1-\langle n_{d\bar{\sigma}}(t)\rangle]+U^{-1}\Omega(\bar{\sigma}t)\}+U\int_0^{-i\beta}d\tau\lambda_{\sigma}(t\tau)R_{\sigma}(\tau t')+\Sigma^{cc}_{dd\sigma}(tt') , \tag{36}$$

where

$$\begin{aligned}\Sigma^{cc}_{dd\sigma}(tt')=&-U\int_0^{-i\beta}d\tau d\tau'\lambda_{\sigma}(t\tau)G_{dd\sigma}(\tau\tau')\Lambda(\bar{\sigma}\tau)G_{dd\sigma}(\tau' t')^{-1}\\&-U\int_0^{-i\beta}d\tau_1 d\tau_2 d\tau d\tau'\lambda_{\sigma}(t\tau_1)\sum_k V_{dk\sigma}(\tau_1)G^0_{k\sigma}(\tau_1\tau_2)G^0_{k\sigma}(\tau_2\tau')V_{kd\sigma}(\tau')G_{dd\sigma}(\tau'\tau)\Lambda(\bar{\sigma}\tau_2)G_{dd\sigma}(\tau t')^{-1} .\end{aligned} \tag{37}$$

This is the basic result of this paper. The iterative solutions of Eq. (26) may be used to evaluate the functional derivatives in the integral equation (37). The result is a nonperturbative solution to the Anderson model. The procedure may be repeated to generate solutions of arbitrary accuracy.

IV. FIRST APPROXIMATION

The simplest solution generated from Eq. (26) corresponds to the Hartree-Fock approximation; it is obtained by neglecting the functional derivatives of $\langle n_{d\bar{\sigma}}\rangle$:

$$G^{\mathrm{HF}}_{dd\sigma}(tt')^{-1}=\left[i\frac{\partial}{\partial t}-E_{d\sigma}(t)-U\langle n_{d\bar{\sigma}}(t)\rangle\right]\delta_{tt'}-S_{\sigma}(tt')\ . \tag{38}$$

The functional derivative terms in Eq. (37) are then to be evaluated using

$$\Lambda(\bar{\sigma}t)G^{\mathrm{HF}}_{dd\sigma}(\tau t')^{-1}=-U[G_{dd\bar{\sigma}}(t't)V_{\bar{\sigma}}(tt')-V^{\dagger}_{\bar{\sigma}}(t't)G_{dd\bar{\sigma}}(tt')]\delta_{t'\tau}\ , \tag{39}$$

where

$$V_{\bar{\sigma}}(tt')=\int d\tau S_{\bar{\sigma}}(t\tau)G_{dd\bar{\sigma}}(\tau t')\ , \tag{40a}$$

$$V^{\dagger}_{\bar{\sigma}}(tt')=\int d\tau G_{dd\bar{\sigma}}(t\tau)S_{\bar{\sigma}}(\tau t')\ . \tag{40b}$$

Therefore, the correction $\Sigma^{cc}_{dd\sigma}$ is

$$\begin{aligned}\Sigma^{cc}_{dd\sigma}(tt')&=U^2\int d\tau\lambda_{\sigma}(t\tau)G_{dd\sigma}(\tau t')[G_{dd\bar{\sigma}}(t'\tau)V_{\bar{\sigma}}(\tau t')-V^{\dagger}_{\bar{\sigma}}(t'\tau)G_{dd\bar{\sigma}}(\tau t')]\\&\quad+U^2\int d\tau_1\,d\tau\,d\tau'\,\lambda_{\sigma}(t\tau_1)\sum_k V_{dk\sigma}(\tau_1)G^0_{k\sigma}(\tau_1\tau)G^0_{k\sigma}(\tau\tau')V_{kd\sigma}(\tau')G_{dd\sigma}(\tau't')\\&\qquad\times[G_{dd\bar{\sigma}}(t'\tau)V-(\tau t')-V^{\dagger}_{\bar{\sigma}}(t'\tau)G_{dd\bar{\sigma}}(\tau t')]\\&=U^2\int d\tau\lambda_{\sigma}(t\tau)\eta_{\sigma}(\tau t')+U^2\int d\tau\sum_k V_{dk\sigma}(t)\kappa_{k\sigma}(\tau)\gamma_{k\sigma}(\tau t')V_{kd\sigma}(t')\ ,\end{aligned} \tag{41}$$

where

$$\eta_{\sigma}(tt')=G_{dd\sigma}(tt')[\,G_{dd\bar{\sigma}}(t't)V_{\bar{\sigma}}(tt')-V^{\dagger}_{\bar{\sigma}}(t't)G_{dd\sigma}(tt')]\ , \tag{42a}$$

$$\kappa_{k\sigma}(tt')=\int d\tau\lambda_{\sigma}(t\tau)G^0_{k\sigma}(\tau t')\ , \tag{42b}$$

$$\gamma_{k\sigma}(tt')=\phi_{k\sigma}(tt')[\,G_{dd\bar{\sigma}}(t't)V_{\bar{\sigma}}(tt')-V^{\dagger}_{\bar{\sigma}}(t't)G_{dd\bar{\sigma}}(tt')]\ , \tag{42c}$$

$$\phi_{k\sigma}(tt')=\int d\tau G^0_{k\sigma}(t\tau)G_{dd\sigma}(\tau t')\ . \tag{42d}$$

This gives for the Fourier components (retarded versions)

$$\Sigma_{dd\sigma}(\omega)=U^2\lambda_{\sigma}(\omega)\times\left[\eta_{\sigma}(\omega)+\sum_k|V_{dk}|^2G^0_{k\sigma}(\omega)\gamma_{k\sigma}(\omega)\right]\ , \tag{43}$$

where

$$\eta_{\sigma}(\omega)=\frac{1}{\beta}\sum_{\omega_\nu}G_{dd\sigma}(\omega_\nu)\psi_{\bar{\sigma}}(\omega-\omega_\nu)$$

$$=\frac{1}{\pi}\int_{-\infty}^{\infty}d\epsilon\{\,\mathrm{Im}\psi_{\bar{\sigma}}(\epsilon)G_{dd\sigma}(\omega-\epsilon)[f^{(-)}(\epsilon)+\tfrac{1}{2}]-\mathrm{Im}G_{dd\sigma}(\epsilon)\psi_{\bar{\sigma}}(\omega-\epsilon)[f^{(+)}(\epsilon)-\tfrac{1}{2}]\}\ , \tag{44a}$$

$$\gamma_{k\sigma}(\omega)=\frac{1}{\beta}\sum_{\omega_\nu}\phi_{k\sigma}(\omega_\nu)\psi_{\bar{\sigma}}(\omega-\omega_\nu)$$

$$=\frac{1}{\pi}\int_{-\infty}^{\infty}d\epsilon\{\,\mathrm{Im}\psi_{\bar{\sigma}}(\epsilon)\phi_{k\sigma}(\omega-\epsilon)[f^{(-)}(\epsilon)+\tfrac{1}{2}]-\mathrm{Im}\phi_{k\sigma}(\epsilon)\psi_{\bar{\sigma}}(\omega-\epsilon)[f^{(+)}(\epsilon)-\tfrac{1}{2}]\}\ . \tag{44b}$$

$\omega_\nu=i\nu\pi/\beta$, ν is an odd integer; $f^{(\pm)}(\epsilon)=(e^{\beta\epsilon}\pm1)^{-1}$,

$$\psi_{\bar{\sigma}}(\omega_B)=-\frac{1}{\beta}\sum_{\omega_\nu}[G_{dd\bar{\sigma}}(\omega_\nu)V_{\bar{\sigma}}(\omega_\nu+\omega_B)-V_{\bar{\sigma}}(\omega_\nu)G_{dd\bar{\sigma}}(\omega_\nu+\omega_B)]$$

$$=\frac{1}{\pi}\int_{-\infty}^{\infty}d\epsilon\{\mathrm{Im}G_{dd\bar{\sigma}}(\epsilon)[V_{\bar{\sigma}}(\epsilon+\omega_B)-V_{\bar{\sigma}}(\epsilon-\omega_B)]-\mathrm{Im}V_{\bar{\sigma}}(\epsilon)[G_{dd\bar{\sigma}}(\epsilon+\omega_B)-G_{dd\bar{\sigma}}(\epsilon-\omega)]\}f^{(+)}(\epsilon) \tag{44c}$$

(ω_B is the Bose frequency).

The sums have been evaluated using the standard methods.[7] The integrals are much easier to evaluate with a square density of states for the metal in the infinite bandwidth limit. For this situation

$$\sum_k|V_{dk}|^2\cdots\to\rho\langle|V_{dk}|^2\rangle_{\mathrm{av}}\int_{-\infty}^{+\infty}d\epsilon\cdots=\frac{\Delta}{\pi}\int_{-\infty}^{+\infty}d\epsilon\cdots\ , \tag{45}$$

where ρ is the constant density of states for the metal. As a further simplification, only zero temperature conditions are considered. Then

$$\sum_k |V_{dk}|^2 \frac{1}{\omega-\epsilon_k}\frac{1}{\omega-\epsilon-\epsilon_k}=0\,, \tag{46a}$$

$$\sum_k |V_{dk}|^2 \frac{1}{\omega-\epsilon_k}\frac{1}{\epsilon-\epsilon_k}=\frac{i\Delta}{\omega-\epsilon}\,, \tag{46b}$$

$$\sum_k |V_{dk}|^2 \frac{1}{\omega-\epsilon_k}=-i\Delta\,, \tag{46c}$$

gives

$$\sum_k |V_{dk}|^2 G^0_{k\sigma}(\omega)\gamma_{k\sigma}(\omega)\equiv Q_\sigma(\omega)=\frac{\Delta}{\pi}\int d\epsilon[\mathrm{Re}G_{dd\sigma}(\epsilon)-i\,\mathrm{Im}G_{dd\sigma}(\epsilon)]\frac{1}{\omega-\epsilon}\psi_{\bar\sigma}(\omega-\epsilon)[f^{(+)}(\epsilon)-\tfrac{1}{2}]\,, \tag{47a}$$

$$\begin{aligned}\psi_{\bar\sigma}(\omega)&=\frac{-\Delta}{\pi}\int d\epsilon\{\mathrm{Im}G_{dd\bar\sigma}(\epsilon)i[G_{dd\bar\sigma}(\epsilon+\omega)+G_{dd\bar\sigma}(\epsilon-\omega)]-\mathrm{Re}G_{dd\bar\sigma}(\epsilon)[G_{dd\bar\sigma}(\epsilon+\omega)-G_{dd\bar\sigma}(\epsilon-\omega)]\}[f^{(+)}(\epsilon)-\tfrac{1}{2}]\\&=-\frac{2\Delta}{\pi(\omega+2i\Delta)}\ln\left[\frac{\omega+i\Delta}{-i\Delta}\right],\quad \beta^{-1}=0\,.\end{aligned} \tag{47b}$$

The last line applies to the symmetric ($E_{d\sigma}=-U/2$, $\langle n_{d\bar\sigma}\rangle=\frac{1}{2}$) case at zero temperature. The remaining integrations must be done numerically.

The spectral density function

$$\begin{aligned}\rho_{d\sigma}(\omega)&=-\frac{1}{\pi}\mathrm{Im}G_{dd\sigma}(\omega+i\delta)\\&=\frac{1}{\pi}\frac{\Delta-\mathrm{Im}\Sigma^c_{dd\sigma}(\omega)}{[\omega-\mathrm{Re}\Sigma^c_{dd\sigma}(\omega)]^2+[\Delta-\mathrm{Im}\Sigma^c_{dd\sigma}(\omega)]^2}\end{aligned} \tag{48}$$

has been computed for the symmetric case. The result is shown in Fig. 1.

V. DISCUSSION

In this paper an alternative expression for the impurity atom's self-energy was presented. While the conventional approach leads to an expansion in U and $G_{dd\sigma}$, the new expression leads to a more complex expansion where the coefficients of $G_{dd\sigma}$ are complicated functions of U and the mixing parameter. The procedure used to obtain this new result is similar to that proposed by Arai and coworkers.[6,10] However, it has an advantage in that it avoids the divergences encountered by Arai and coworkers[6,10] in their solution. Another distinction is that any correction generated from Eq. (37) will vanish in the limit $U\to 0$ and in the limit $V_{dk}\to 0$. This means that $G_{dd\sigma}$ is exact in these limits. As the procedure employed in this paper is effectively a systematic decoupling scheme this is not unusual, since most decoupling schemes have this property. In fact, if the correction term in Eq. (36) is neglected, one gets the decoupling approximation obtained by Kemeny[11] [note that $\Omega(\bar\sigma t)=0$ for $\hat E_{d\bar\sigma},\hat V_{\bar\sigma}=0$]. Therefore, the choice for $\hat S$ given by Eq. (19) allows one to make systematic corrections to Kemeny's approximation in the same way that one makes corrections to the Hartree-Fock approximation. It is also possible to derive a correction[12] term for the decoupling scheme employed by Hewson.[13] However, Hewson's approximation is much cruder than Kemeny's.

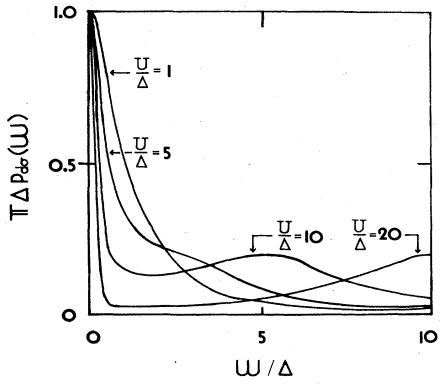

FIG. 1. Spectral density $\rho_{d\sigma}(\omega)$ vs ω for several values of U/Δ.

As a first approximation, the simplest solution to the integral equation (26) was used to evaluate the functional derivatives in the new self-energy equation (37). The result was used to calculate the spectral density function for the symmetric case at zero temperature (Fig. 1). The results are consistent with the fourth order in the U calculation of Yamada.[9]

The integral equation (37) may also be solved iteratively independently of Eq. (26). However, this leads to terms proportional to

$$\bar V\langle c^\dagger_{d\bar\sigma}B_{\bar\sigma}\rangle=\frac{1}{\pi i}\int_{-\infty}^{+\infty}d\omega\,\mathrm{Im}[S_{\bar\sigma}(\omega)G_{dd\bar\sigma}(\omega)]f^{(+)}(\omega)\,, \tag{49}$$

which diverges in the infinite bandwidth limit at zero temperature. The iterative solutions of Eq. (26) are not restricted to a finite bandwidth. This is the motivation for suggesting that it be used to evaluate the functional derivatives in Eq. (37). This is not meant to imply that the iterative solutions of Eq. (37) are not interesting. It leads to some interesting results which will be presented in a future paper.

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[1]P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[2]G. Grüner and A. Zawadowski, Rep. Prog. Phys. **37**, 1497 (1974).
[3]*Valence Fluctuations in Solids,* edited by L. M. Falicov, W. Hanke, and B. Maple (North-Holland, Amsterdam, 1981).
[4]T. L. Einstein, J. A. Hertz, and J. R. Schrieffer, in *Theory of Chemisorption,* Vol. 19 of *Topics in Current Physics,* edited by J. R. Smith (Springer, New York, 1980).
[5]F. C. Zhang and T. K. Lee, Phys. Rev. B **30**, 1556 (1984).
[6]Tadashi Arai and J. W. Garland, Phys. Rev. Lett. **50**, 378 (1983).
[7]L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (Benjamin, New York, 1962).
[8]K. Schönhammer, Solid State Commun. **22**, 51 (1977).
[9]Kosaku Yamada, Prog. Theor. Phys. **53**, 970 (1975).
[10]Tadashi Arai, Morrel H. Cohen, and M. P. Tosi, Phys. Rev. B **15**, 1817 (1977).
[11]G. Kemeny, Phys. Rev. **150**, 459 (1966).
[12]Henry L. Neal, Ph.D. thesis, Howard University, 1984.
[13]A. C. Hewson, Phys. Rev. **144**, 420 (1966).