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# Nonperturbative approach to the Newns-Anderson model of chemisorption

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A functional-derivative Green's-function solution of the Anderson model, obtained in a previous paper [Phys. Rev. B **32**, 5002 (1985)], is discussed in the context of chemisorption theory. The short-chain model is used to make comparisons with the best of previous solutions. The functional-derivative solution yields exact results in the electron-hole-symmetric zero-bandwidth limit and interpolates accurately between the weak-binding and rebonded-surface-complex limits.

Since the work of Newns,[1] the Anderson[2] model has been applied to chemisorption theory by many researchers.[3–6] A variety of solutions and methods for obtaining them have been reported. Notable among these are the solutions given by Brenig and Schönhammer[4] and by Baldo *et al.*[5] These solutions are marked by their simplicity and accuracy. The Hamiltonian under consideration is

$$H=\sum_{k,\sigma}E_{k\sigma}C^{\dagger}_{k\sigma}C_{k\sigma}+\sum_{\sigma}(E_{d\sigma}n_{d\sigma}+\tfrac{1}{2}Un_{d\sigma}n_{d\bar{\sigma}})+\sum_{k,\sigma}(V_{dk}C^{\dagger}_{d\sigma}C_{k\sigma}+V_{kd}C^{\dagger}_{k\sigma}C_{d\sigma})\ , \tag{1}$$

where $n_{d\sigma}=C^{\dagger}_{d\sigma}C_{d\sigma}$, $C^{\dagger}_{k\sigma}$ ($C_{k\sigma}$) creates (destroys) electrons in the single-particle states of the host, $k$ denotes the relevant quantum numbers, $\sigma$ denotes the spin ($\bar{\sigma}=-\sigma$), and $d$ denotes the adatom state. The first term describes the host, the second term describes the adatom with intra-atom Coulomb repulsion energy $U$, and the last term describes the host-adatom interaction. In the renormalization-group[7] and Bethe-ansatz[8] solutions, the form of the parameters $E_{k\sigma}$ and $V_{dk\sigma}$ is usually chosen to be very simple. Thus these solutions are not generally applicable to chemisorption theory, where it may be important to retain some of the complexity involving these parameters.

In a previous paper[9] (hereafter referred to as paper I) we presented a solution that gives very accurate results for the simple form of the parameters. The solution was obtained without making any simplifying assumptions regarding the parameters. In this paper we demonstrate that this solution also gives very accurate results in the context of chemisorption theory. Important features of this solution and the procedure[9–11] used to obtain it are that it preserves the conservation laws[11] (of particle number, momentum, and energy) and may be applied at temperatures above absolute zero. Furthermore, this solution is amenable to a procedure for systematic corrections.[9]

For the sake of clarity, in this paper, we repeat some of the results and equations of paper I. In paper I an exact expression [Eq. (36)] for the self-energy $\Sigma_{dd\sigma}$ of the Anderson model was derived using the functional-derivative technique.[10,11] This equation was solved approximately by evaluating the functional derivatives [in Eq. (37)] with the Hartree-Fock solution for the adatom Green's function $G_{dd\sigma}$. The result is

$$\Sigma_{dd\sigma}(\omega)=U\langle n_{d\bar{\sigma}}\rangle+U^2\lambda_\sigma(\omega)\langle n_{d\bar{\sigma}}\rangle[1-\langle n_{d\bar{\sigma}}\rangle]+\Sigma^{cc}_{dd\sigma}(\omega)\ , \tag{2}$$

where $\langle\cdots\rangle$ denotes the thermodynamic average. The self-energy correction $\Sigma^{cc}_{dd\sigma}$ is

$$\Sigma^{cc}_{dd\sigma}(\omega)=U^2\lambda_\sigma(\omega)\left[\eta_\sigma(\omega)+\sum_k|V_{dk}|^2G^0_{k\sigma}(\omega)\gamma_{k\sigma}(\omega)\right]\ , \tag{3}$$

$$\lambda_\sigma(\omega)=[\omega-E_{d\sigma}-U(1-\langle n_{d\bar{\sigma}}\rangle)-S_\sigma(\omega)]^{-1}\ , \tag{4}$$

$$S_\sigma(\omega)=\sum_k|V_{dk}|^2G^0_{k\sigma}(\omega)\ , \tag{5}$$

$$G^0_{k\sigma}(\omega)=(\omega-E_{k\sigma})^{-1}\ . \tag{6}$$

Equation (3) is Eq. (43) of paper I. The quantities $\eta_\sigma(\omega)$ and $\gamma_{k\sigma}(\omega)$ are determined by sums over the Fermi frequencies $\omega_\nu = 2\pi i \nu/\beta$, where $\nu$ is an odd integer and $\beta$ is the inverse temperature:

$$\eta_\sigma(\omega)=\frac{1}{\beta}\sum_{\nu} G^{\mathrm{HF}}_{dd\sigma}(\omega_\nu)\psi_{\bar\sigma}(\omega-\omega_\nu) , \tag{7}$$

$$\gamma_{k\sigma}=\frac{1}{\beta}\sum_{\nu} \phi_{k\sigma}(\omega)\psi_{\bar\sigma}(\omega-\omega_\nu) , \tag{8}$$

$$\phi_{k\sigma}(\omega)=G^{0}_{k\sigma}(\omega)G^{\mathrm{HF}}_{dd\sigma}(\omega) , \tag{9}$$

$$\psi_\sigma(\omega_B)=\frac{1}{\beta}\sum_{\nu}[G^{\mathrm{HF}}_{dd\sigma}(\omega_\nu)V_{\bar\sigma}(\omega_\nu+\omega_B) - G^{\mathrm{HF}}_{dd\sigma}(\omega_\nu+\omega_B)V_{\bar\sigma}(\omega_\nu)] , \tag{10}$$

$\omega_B$ is a Bose frequency,

$$V_\sigma(\omega)=S_\sigma(\omega)G^{\mathrm{HF}}_{dd\sigma}(\omega) , \tag{11}$$

$G^{\mathrm{HF}}_{dd\sigma}(\omega)$ is the Hartree-Fock Green's function:

$$G^{\mathrm{HF}}_{dd\sigma}(\omega)=[\omega-E_{d\sigma}-U\langle n_{d\bar\sigma}\rangle-S_\sigma(\omega)]^{-1} . \tag{12}$$

Equation (3) yields exact results in the limits $U\rightarrow 0$ for arbitrary $V_{dk}$, $V_{dk}\rightarrow 0$ for arbitrary $U$,[9] and $E_{k\sigma}\rightarrow 0$ for arbitrary $U$ and $V_{dk}$ (zero-bandwidth limit).

For calculational simplicity we restrict our discussion to the symmetric case ($E_{d\sigma}=-U/2$ and $\langle n_{d\sigma}\rangle=\langle n_{d\bar\sigma}\rangle=\frac{1}{2}$) at zero temperature.

First we consider the zero-bandwidth limit ($E_{k\sigma}=0$). Equation (3) becomes

$$\Sigma^{cc}_{dd\sigma}(\omega)=U^2\lambda_\sigma(\omega)[\eta_\sigma(\omega)+\bar V^2\gamma_\sigma(\omega)/\omega] , \tag{13}$$

where the quantities $\bar V$, $\lambda_\sigma(\omega)$, $\eta_\sigma(\omega)$, and $\gamma_\sigma(\omega)$ are given, respectively, by

$$\bar V=\left[\sum_k |V_{dk}|^2\right]^{1/2} , \tag{14}$$

$$\lambda_\sigma(\omega)=\frac{\omega}{\omega^2-\bar V^2} , \tag{15}$$

$$\eta_\sigma(\omega)=\frac{3}{2}\frac{\bar V^2}{(\omega^2-9\bar V^2)} , \tag{16}$$

$$\gamma_\sigma(\omega)=\frac{1}{2}\frac{\omega}{(\omega^2-9\bar V^2)} . \tag{17}$$

From Eq. (2) this gives

$$\Sigma_{dd\sigma}(\omega)=U/2+\frac{U^2}{4}\frac{\omega}{(\omega^2-9\bar V^2)} , \tag{18}$$

which is exact. The same result was obtained by the method of Baldo *et al.*[5]

We now consider the case of an adatom adsorbed at one end of a chain of three host atoms.[12] The Hamiltonian for this system is

$$H=-T\sum_{i,\sigma}(C^{\dagger}_{i\sigma}C_{i+1,\sigma}+\mathrm{H.c.}) + \sum_{\sigma}(E_{d\sigma}n_{d\sigma}+\tfrac{1}{2}Un_{d\sigma}n_{d\bar\sigma}) - V\sum_{\sigma}(C^{\dagger}_{1\sigma}C_{d\sigma}+\mathrm{H.c.}) \tag{19}$$

and may be transformed[6,12] into Eq. (1) as follows:

$$E_{k\sigma}=-\sqrt{2}T,0,\sqrt{2}T , \tag{20}$$

$$V_{dk}=V/2,V/\sqrt{2},V/2 . \tag{21}$$

The self-energy may be determined analytically using the standard techniques[11,13] for evaluating the frequency sums. Then the Green's function is written as

$$G_{dd\sigma}(\omega)=\sum_q \frac{A^q}{\omega-x_q} =[\omega-E_{d\sigma}-S_\sigma(\omega)-\Sigma_{dd\sigma}(\omega)]^{-1} , \tag{22}$$

where the poles $x_q$ generally must be determined numerically. The extension to temperatures greater than absolute zero is straightforward as all of the above equations are applicable at all temperatures.

Figure 1 shows the results of our calculation. We have calculated the chemisorption energy $\Delta E$ as a function of $V$ using the well-known formula[14]

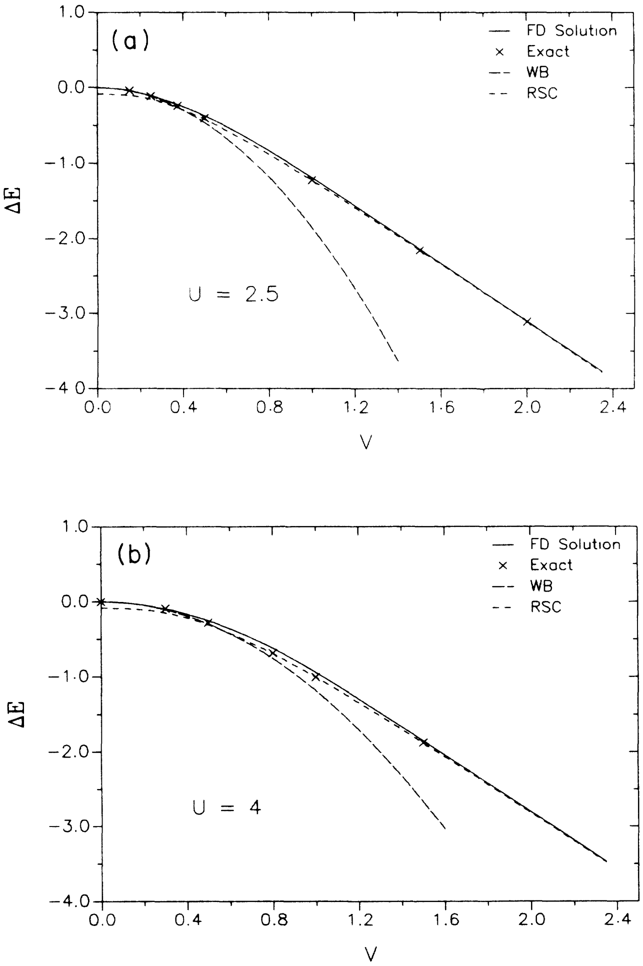

FIG. 1. $\Delta E$ vs $V$ for (a) $U=2.5$ and (b) $U=4.0$, all in units of 2 T. The exact points are from Ref. 12.

$$\Delta E = \frac{1}{4\pi i}\sum_{\sigma}\int_C dz\left[ z + E_{d\sigma} + S_\sigma(z) - 2z\frac{\partial}{\partial z}S_\sigma(z)\right] G_{dd\sigma}(z) - \sum_{\sigma}(1-\langle n_{d\bar{\sigma}}\rangle_0)E_{d\sigma}\ , \tag{23}$$

where $C$ is a contour that includes the real axis and is closed in the upper half of the complex $z$ plane, and $\langle \cdots \rangle_0$ denotes the thermodynamic average at $V=0$. Our approximate functional-derivative (FD) solution is compared with the weak-binding (WB), rebonded surface complex (RSC), and exact numerical results reported by Einstein.[12] The FD results clearly show good agreement in the transition region between the WB and RSC limits.

In summary, the FD solution interpolates accurately between the weak-coupling and strong-coupling limits and yields exact results in the zero-bandwidth limit. The interpolating schemes[4,5] typically give slightly more accurate results[15] for the ground-state energy and the quasiparticle spectrum in the transition region than the FD solution considered here. However, such schemes are typically not easily extended to temperatures above absolute zero and are generally not amenable to systematic corrections as is the FD solution.[9] We believe that the FD solution should serve as a useful complement to the many solutions available in the literature.

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