A new diagram technique for the Anderson model

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Abstract. Using the perturbation expansion in the rebonding interaction near the surface molecule limit, a new diagram technique for the Anderson model is proposed. The expression for the self-energy in the second order in the rebonding interaction is obtained. Approximate expressions for the self-energy beyond the second order are suggested. The quasiparticle spectrum for the finite-chain model is calculated and compared with the exact results and others in the literature.

1. Introduction

Many-body effects play an important role in adsorption phenomena on transition metals. Considerable progress has been achieved in the understanding of these effects based on the Anderson–Newns model and using a variety of approaches. In particular, a number of important results has been obtained for the adatom or impurity density of states (see, e.g., the review article [1] and the more recent papers [2–6]). The traditional perturbation methods for the Anderson model use expansion in the hybridization or the Coulomb repulsion. However, for the hydrogen chemisorption problem the hopping parameter, the Coulomb repulsion and the bandwidth have the same order of magnitude so expansions in the hybridization and the Coulomb repulsion as well as a number of decoupling methods are not fully regular procedures. The more recent theoretical methods have been mainly elaborated for the magnetic impurity problem. On the other hand, the hydrogen chemisorption problem is characterized by the finite bandwidth, nondegenerate electron level of an adatom and the possibility of the existence of bonding and antibonding levels outside the substrate energy band.

In [7] the one-level impurity Green function has been calculated exactly for finite bandwidth in the limit when the substrate has a completely filled (or empty) energy band. In [8] we obtained the exact adatom density of unoccupied states (or the exact adatom density of occupied states) for a transition metal with an almost filled (or almost empty) energy band. For these cases the exact dynamic form factor of chemisorbed hydrogen has also been calculated [9]. However, in the general case the substrate energy band is not almost filled or almost empty and one needs in an approximate treatment of the Anderson impurity model.

Unlike conventional theoretical investigations, we use the perturbation expansion in the rebonding interaction near the surface molecule (SM) limit, which is more appropriate for the chemisorption problem [10]. The analogous perturbation expansion can also be used for the magnetic impurity problem in the case when the impurity atom interacts strongly with the narrow-band alloy. It seems worthwhile to test the known problem by the new method

and compare our results with others in the literature. As the SM Hamiltonian contains the Coulomb interaction on an adatom, there exists no ordinary Wick theorem leading to a straightforward diagrammatic analysis. In order to overcome this difficulty, in [11] we formulated the generalized Wick theorem for the Anderson model. Using this theorem, a new diagram technique for the temperature Green function and the thermodynamic potential has been proposed [11]. Having proved the applicability of the new diagram technique [11], we present here a simple method for its construction: namely, we consider the sum of the Coulomb term and the rebonding interaction as a perturbation and use the ordinary Wick theorem. After that we sum the class of diagrams of a given order in the rebonding interaction over all orders in the Coulomb repulsion. As a result, we obtain the diagram technique of [11]. The analogous method of construction of the diagram technique for the calculation of the chemisorption energy has been proposed in [12].

The perturbation expansion in the rebonding interaction has already been used in [13–15] for calculation of chemisorption energy up to second order within different models of the chemisorption process. An approximate expression for the self-energy for the symmetric strong-coupling case has been obtained in [16]. Below we present the complete expression for the self-energy in second order in the rebonding interaction. The approximate expressions for the self-energy beyond second order are also suggested. To check the accuracy of our expressions, we calculate the adatom density of states and the chemisorption energy for the finite-chain model of adsorption [14] and compare our results with the exact ones and the rather accurate results of [17]. The physical nature of the characteristic features of the adatom density of states is discussed in terms of the transitions between the energy levels of the SM.

2. The perturbation expansion near the surface molecule limit

The Anderson Hamiltonian has the form

$$H = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\sigma}(\varepsilon_a n_{a\sigma} + \tfrac{1}{2}U n_{a\sigma} n_{a-\sigma}) + \sum_{k,\sigma}(V_{ak}c_{a\sigma}^+ c_{k\sigma} + \text{HC}). \qquad (1)$$

We employ here the standard notations [18]; energies of single-particle states are measured relative to the centre of the substrate energy band; the energy unit is given by $B/2$ where B is the bandwidth; $V = (\sum_k |V_{ak}|^2)^{1/2}$. From (1) it follows that the hydrogen 1s state couples directly only with the normalized state

$$|b\rangle = V^{-1} \sum_k V_{ak}^* |k\rangle \qquad (2)$$

introduced in [16]. Therefore instead of the basis set $|k\rangle$ we consider the equivalent basis set constructed of the state $|b\rangle$ and normalized states $|p\rangle$ which are orthogonal to $|b\rangle$ and to each other. Let $c_{b\sigma}^+$, $c_{b\sigma}$ and $c_{p\sigma}^+$, $c_{p\sigma}$ be the creation and annihilation operators of an electron in these states. Thus, we have the next canonical transformation:

$$c_{b\sigma}^+ = \sum_k u_{0k}^* c_{k\sigma}^+ \qquad c_{p\sigma}^+ = \sum_k u_{pk}^* c_{k\sigma}^+ \qquad (3)$$

where $u_{0k}^* = V_{ak}^*/V$, $p \neq 0$ and the coefficients $u_{nk}(n = 0, p)$ satisfy the conditions

$$\sum_k u_{nk} u_{n'k}^* = \delta_{nn'}. \qquad (4)$$

Then the Anderson Hamiltonian (1) can be rewritten in the form

$$H = H_{sm} + H_{rm} + \Delta H. \qquad (5)$$

Here H_{sm} is the Hamiltonian of the a–b SM

$$H_{sm} = \sum_{\sigma} \{\varepsilon_a n_{a\sigma} + \varepsilon_b n_{b\sigma} + 1/2 U n_{a\sigma} n_{a-\sigma} + V(c_{a\sigma}^+ c_{b\sigma} + \text{HC})\} \tag{6}$$

$\varepsilon_b = V^{-2} \sum_k \varepsilon_k |V_{ak}|^2$ is the energy of the state $|b\rangle$

$$H_{rm} = \sum_{k,\sigma} \sum_{p,p'} \varepsilon_k u_{pk} u_{p'k}^* c_{p\sigma}^+ c_{p'\sigma} \tag{7}$$

is the Hamiltonian of the remaining metal, i.e. the metal from which the state $|b\rangle$ is detached, and

$$\Delta H = \sum_{k,\sigma} \sum_{p} \varepsilon_k u_{pk} u_{0k}^* c_{p\sigma}^+ c_{b\sigma} + \text{HC} \tag{8}$$

is the rebonding interaction which describes the rebonding of SM to the remaining metal.

Further on, we choose the coefficients u_{pk} of the canonical transformation (3) in such a way that the states $|p\rangle$ will be the eigenstates of the Hamiltonian H_{rm}. The analogous problem has been considered in [19] for the Kondo model. For this purpose H_{rm} should be diagonalized under the condition (4) or, equivalently, we have to find values of u_{pk} which minimize the function [15, 19]

$$E = \sum_{k,p} \varepsilon_k |u_{pk}|^2 - 2 \sum_{k,p} \lambda_p |u_{pk}|^2 - \sum_{k,p} (\mu_p u_{pk} u_{0k}^* + \mu_p^* u_{pk}^* u_{0k}). \tag{9}$$

Here λ_p and μ_p are Lagrange multipliers. Taking the derivative with respect to u_{pk}^*, one obtains [15, 19]

$$u_{pk} = \mu_p V_{ak} / [2(\varepsilon_k - \lambda_p) V]. \tag{10}$$

Then the Lagrange multipliers λ_p and μ_p are determined from the conditions (4) and are given by the equations [15, 19]

$$\sum_k \frac{|V_{ak}|^2}{\varepsilon_k - \lambda_p} = 0 \qquad \frac{|\mu_p|^2}{4} = V^2 \left[\sum_k \frac{|V_{ak}|^2}{(\varepsilon_k - \lambda_p)^2} \right]^{-1}. \tag{11}$$

It can be shown [15] that $\sum_k \varepsilon_k u_{pk} u_{p'k}^* = \lambda_p \delta_{pp'}$, $\sum_k \varepsilon_k u_{pk} u_{0k}^* = \mu_p / 2$, and, finally, the Anderson Hamiltonian takes the form [15]

$$H = H_{sm} + \sum_{p,\sigma} \lambda_p c_{p\sigma}^+ c_{p\sigma} + \Delta H \tag{12}$$

where the rebonding interaction ΔH is given by

$$\Delta H = \sum_{p,\sigma} \left(\frac{\mu_p}{2} c_{p\sigma}^+ c_{b\sigma} + \text{HC} \right). \tag{13}$$

From (12) and (13) it follows that λ_p has the physical meaning of the energy of an electron in the single-particle state $|p\rangle$ of the remaining metal and $\mu_p/2$ is the hopping parameter between the states $|p\rangle$ and $|b\rangle$. The energies λ_p and μ_p enter the diagrams for the Green functions only through the function $\chi(z)$ defined below.

In the case of the one-level impurity embedded in the narrow-band alloy the Hamiltonian (6) can be treated as the Hamiltonian of the strong-coupling complex consisting of the impurity and the localized state $|b\rangle$. For the chemisorption problem the state $|b\rangle$ has the physical meaning of the group orbital [1], which is localized in the neighbourhood of the adatom.

Below the diagram technique is constructed for the temperature Green function $\mathcal{L}_{ij\sigma}(\beta_1, \beta_2) = -\langle T c_{i\sigma}(\beta_1) \bar{c}_{j\sigma}(\beta_2) \rangle$ where $i, j = a, b$. The Green function $G_{ij\sigma}(\beta_1, \beta_2)$

corresponds to the case $\Delta H = 0$. Let $\mathcal{L}_{ij\sigma}(\varepsilon_F + i\omega)$ and $G_{ij\sigma}(\varepsilon_F + i\omega)$ be the Fourier transforms of $\mathcal{L}_{ij\sigma}(\beta_1, \beta_2)$ and $G_{ij\sigma}(\beta_1, \beta_2)$ in the limit $T \to 0$. The retarded Green function $\mathcal{L}_{ij\sigma}^r(\varepsilon)$ is equal to $\mathcal{L}_{ij\sigma}(\varepsilon + i0)$ where $\mathcal{L}_{ij\sigma}(z)$ is the analytic continuation of $\mathcal{L}_{ij\sigma}(\varepsilon_F + i\omega)$ from the line segment $\mathrm{Re}\, z = \varepsilon_F$, $0 < \mathrm{Im}\, z < \infty$ to the upper half of the complex plane. The sum of the Coulomb repulsion $\sum_\sigma 1/2 U n_{a\sigma} n_{a-\sigma}$ and the rebonding interaction ΔH (13) is considered as a perturbation so that nonperturbed Green functions $g_{ij\sigma}(\beta_1, \beta_2)$, $g_{ip\sigma}(\beta_1, \beta_2)$ and $g_{pp\sigma}(\beta_1, \beta_2) = G_{pp\sigma}(\beta_1, \beta_2)$ correspond to the case $U = 0$, $\Delta H = 0$. If we use the ordinary Wick theorem and perform the well known partial summation of diagrams, the lines of Green functions $g_{ij\sigma}(z)$ are changed to heavy lines $G_{ij\sigma}(z)$. Then the Green function $\mathcal{L}_{ij\sigma}(z)$ is equal to the sum of the contributions of the connected diagrams which include (i) the heavy lines of Green functions $G_{ij\sigma}(z)$ which take into account the effect of the electron–electron interaction, (ii) the lines of the Coulomb interaction U and (iii) n vertices $\mu_p/2$ or $\mu_p^*/2$ for each diagram of order n in ΔH. Since $g_{ap\sigma} = g_{bp\sigma} = 0$, $G_{pp'\sigma} = \delta_{pp'} G_{pp\sigma}$, we have $n = 2k$, and $\mu_p/2$-vertices subdivide in pairs connected by the lines $G_{pp\sigma}(z)$. Thus, the Green function $G_{pp\sigma}$ enters the diagrams only in the combination $\chi(z) = \sum_p G_{pp\sigma}(z)|\mu_p|^2/4$. The temperature Green function $G_{pp\sigma}(z)$ coincides with the temperature Green function of the free electron $G_{pp\sigma}(z) = (z - \lambda_p)^{-1}$.

From (11) it follows that the energies λ_p are the zeros of the function $\Lambda(z) = (\pi V^2)^{-1} \sum_k |V_{ak}|^2/(z - \varepsilon_k)$ and $|\mu_p|^2/4 = -[\pi \, d\Lambda\,(\lambda_p)\, d\lambda]^{-1}$. Then for arbitrary z with $\mathrm{Im}\, z \neq 0$ we have

$$\chi(z) = -\frac{1}{2\pi i}\frac{1}{\pi}\oint_l \frac{dz'}{\Lambda(z')(z - z')} - [\pi\Lambda(z)]^{-1} \tag{14}$$

where the contour l encloses the point z and all points λ_p. When $|z'| \to \infty$, $\Lambda(z') \approx (1/z' + \varepsilon_b/(z')^2)/\pi$ and for the contour l of a large radius the first term in the right-hand side of (14) is equal to $z - \varepsilon_b$. Thus,

$$\chi(z) = z - \varepsilon_b - [\pi\Lambda(z)]^{-1}. \tag{15}$$

If we define the function $\varphi(\varepsilon) = -\mathrm{Im}\,\chi(\varepsilon + i0) = \mathrm{Im}[\pi\Lambda(\varepsilon + i0)]^{-1}$, then

$$\varphi(\varepsilon) = \pi^{-1}\Delta(\varepsilon)/[\Delta^2(\varepsilon) + \Lambda^2(\varepsilon)]. \tag{16}$$

Here $\Delta(\varepsilon)$ is the electronic density of states of the substrate projected into the orbital $|b\rangle$ and $\Lambda(\varepsilon)$ is its Hilbert transform. In the limit of the macroscopically large volume of the substrate $\Lambda(z)$ is the analytic continuation of $\Lambda(\varepsilon)$ from the interval $(0, \infty)$ of the real axis to the complex plane with the cut $[-1, 1]$.

From the equations of motion it can be shown that

$$G_{ba\sigma} = G_{ab\sigma} \qquad G_{ab\sigma}(z) = V G_{aa\sigma}(z)/(z - \varepsilon_b)$$
$$G_{bb\sigma}(z) = 1/(z - \varepsilon_b) + V^2 G_{aa\sigma}(z)/(z - \varepsilon_b)^2. \tag{17}$$

For the Green function $G_{aa\sigma}(z)$ we have

$$G_{aa\sigma}(z) = [z - \varepsilon_a - \Sigma_0(z) - V^2\pi\Lambda_0(z)]^{-1} \tag{18}$$

where $\Lambda_0(z) = [\pi(z - \varepsilon_b)]^{-1}$ and the self-energy $\Sigma_0(z)$ for the symmetric case $\varepsilon_a = -U/2$ is given by the equation [17]

$$\Sigma_0(z) = U/2 + M_0(z) \qquad M_0(z) = U^2 z/[4(z^2 - 9V^2)]. \tag{19}$$

For the general case the nonelectrostatic part of the self-energy $M_0(z)$ is given in [20].

In figure 1 we show the diagrammatic representation of the Green function $\mathcal{L}_{aa\sigma}(z)$ up to fourth order in the rebonding interaction. The Green function $G_{ij\sigma}(z)$ are depicted as straight heavy lines. The ends of a line are marked by indices i and j. A dashed
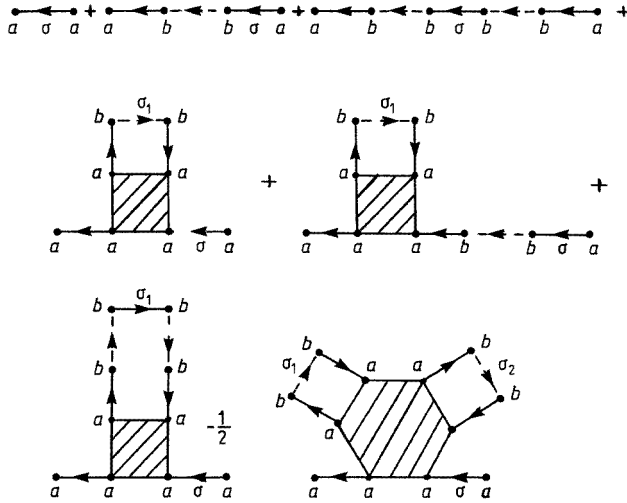
Figure 1. A diagrammatic representation of the adatom Green function up to fourth order in the rebonding interaction.

line corresponds to the function $\chi(z)$. This function describes the effective contribution of electrons propagating in the states p. The first three diagrams of figure 1 do not include explicitly the lines of the Coulomb interaction U. The diagrams which include these lines can be summed in all orders in U giving the other diagrams of figure 1 as the result. n-sided shaded polygons depict the vertex functions Γ_k which depend on the electron–electron interaction. Here $k = n/2$ and $\Gamma_k \equiv 0$ for $U = 0$. As is obvious from the diagrammatic point of view and can also be shown analytically [11], the vertex functions Γ_k are expressed through the Kubo cumulants [21] G_k where the subscript k indicates that the cumulants G_k originate from the k-particle adatom Green functions. For example,

$$\Gamma_{2,\sigma\sigma 1}(z, z_1, z_2) = G_{2,\sigma\sigma 1}(z, z_1, z_2)[G_{aa\sigma}(z)G_{aa\sigma 1}(z_1)G_{aa\sigma}(z + z_1 - z_2)G_{aa\sigma 1}(z_2)]^{-1} \quad (20)$$

where $G_{2,\sigma\sigma 1}(z, z_1, z_2)$ is the Fourier transform of the Kubo cumulant

$$\begin{aligned}
G_2(\sigma\tau, \sigma_1\tau_1, \sigma\tau', \sigma_1\tau_2) &= \langle T c_{a\sigma}(\tau)c_{a\sigma 1}(\tau_1)\bar{c}_{a\sigma}(\tau')\bar{c}_{a\sigma 1}(\tau_2)\rangle \\
&\quad -\delta_{\sigma\sigma 1}G_{aa\sigma}(\tau - \tau_2)G_{aa\sigma}(\tau_1 - \tau') + G_{aa\sigma}(\tau - \tau')G_{aa\sigma 1}(\tau_1 - \tau_2). \quad (21)
\end{aligned}$$

Here the brackets $\langle \ldots \rangle$ denote the average over the ground state of the doubly occupied SM.

The diagrams of figure 1 represent also the expansion of the Green function $\mathcal{L}_{aa\sigma}(z)$ in the hybridization. In this case $b = a$, $\chi(z)$ is replaced by $\Gamma(z) = \pi V^2 \Lambda(z)$, the Green function $G_{aa\sigma}(z)$ is replaced by its limit for $V \to 0$ and the brackets in (21) denote the average over the ground state of the isolated adatom.

The diagrams of figure 1 for $\mathcal{L}_{aa\sigma}(z)$ and the analogous diagrams for the Green function $\mathcal{L}_{ba\sigma}(z)$ lead to the next Dyson equations:

$$\mathcal{L}_{aa\sigma}(z) = G_{aa\sigma}(z) + G_{ab\sigma}(z)\chi(z)\mathcal{L}_{ba\sigma}(z) + G_{aa\sigma}(z)\Delta\Sigma(z)\mathcal{L}_{aa\sigma}(z) \quad (22)$$

$$\mathcal{L}_{ba\sigma}(z) = G_{ba\sigma}(z) + G_{bb\sigma}(z)\chi(z)\mathcal{L}_{ba\sigma}(z) + G_{ba\sigma}(z)\Delta\Sigma(z)\mathcal{L}_{aa\sigma}(z). \quad (23)$$

From these equations and expressions (15)–(18) we obtain

$$\mathcal{L}_{aa\sigma}(z) = [z - \varepsilon_a - \Sigma_0(z) - \Delta\Sigma(z) - \pi V^2 \Lambda(z)]^{-1} \quad (24)$$

$$\mathcal{L}_{ba\sigma}(z) = \pi V \Lambda(z)\mathcal{L}_{aa\sigma}(z). \quad (25)$$

The diagrams which give the contribution to $\Delta\Sigma(z)$ are easily extracted from figure 1. In particular, the second-order contribution $\Delta\Sigma^{(2)}$ to $\Delta\Sigma$ is given by the equation

$$\Delta\Sigma^{(2)}(z) = -i/(2\pi)\Sigma_{\sigma'}\int_l \Gamma_{2,\sigma\sigma'}(z,z',z')G_{ab\sigma'}(z')\chi(z')G_{ba\sigma'}(z')\,dz' \quad (26)$$

where the integration is performed over the line l: $\mathrm{Re}\,z' = \varepsilon_F$ in the complex plane with the cut $[-1,1]$. We present here the expression for $\Delta\Sigma^{(2)}$ only for the symmetric case $\varepsilon_a = -U/2$, $\varepsilon_F = 0$, $\varphi(\varepsilon) = \varphi(-\varepsilon)$:

$$\Delta\Sigma^{(2)}(z) = -\frac{24x^2V^2z}{\pi(z^2-9V^2)^2}\int_{-1}^{0}\frac{R(z,\varepsilon)\varphi(\varepsilon)\,d\varepsilon}{P(z,\varepsilon)(\varepsilon+d_1)^2(\varepsilon+d_2)^2} \quad (27)$$

where $x = U/4$, $r = (x^2+4V^2)^{1/2}$, $d_1 = -r + (x^2+V^2)^{1/2}$, $d_2 = -r - (x^2+V^2)^{1/2}$,

$$\begin{aligned}
R(z,\varepsilon) = \ &3\varepsilon^6 - 24r\varepsilon^5 - [5z^2 - 36(2x^2+9V^2)]\varepsilon^4 + 4r[7z^2 - 3(8x^2+49V^2)]\varepsilon^3 \\
&+[2z^4 - 2(30x^2+121V^2)z^2 + 3(16x^4+256x^2V^2+803V^4)]\varepsilon^2 \\
&-4[2(x^2+3V^2)z^4 - (16x^4+121x^2V^2+240V^4)z^2 \\
&+3V^2(20x^4+191x^2V^2+438V^4)]\varepsilon/r + 2(4x^2+9V^2)z^4 \\
&-(32x^4+200x^2V^2+369V^4)z^2 + 108V^4(3x^2+11V^2)
\end{aligned} \quad (28)$$

$$P(z,\varepsilon) = (z+\varepsilon+d_{21})(z-\varepsilon-d_{21})(z+\varepsilon+d_t)(z-\varepsilon-d_t). \quad (29)$$

It is known [22] that the doubly occupied SM has three singlet states $|20\rangle$, $|21\rangle$ and $|22\rangle$ with the energies E_{20}, E_{21} and E_{22} and three triplet states with equal energies $E_t = \varepsilon_a + \varepsilon_b$. In (29) $d_{21} = E_{20} - E_{21} = -x - r$ and $d_t = E_{20} - E_t = x - r$. The state $|22\rangle$ does not contribute to $P(z,\varepsilon)$ in the symmetric case. At the same time for the symmetric case $d_{21} = E_{20} - E_4 = E_{20} - E_0$ where E_4 and E_0 are the energies of an SM having four and zero electrons, respectively. Using the Lehmann representation for the Green function $\mathcal{L}_{aa\sigma}(z)$, we conclude that the contribution $\Delta\Sigma^{(2)}$ to $\Delta\Sigma$ is caused by the transitions from the perturbed ground state of the doubly occupied SM to the state $|21\rangle$, the triplet states and the states of SM with four and zero electrons plus an extra electron or hole within the remaining metal.

If we substitute the Green function $\mathcal{L}_{aa\sigma}(z)$ with $\Delta\Sigma = \Delta\Sigma^{(2)}$ into the equation of [23] for the binding energy, then to second order in the rebonding interaction we obtain an expression identical to that obtained in [15] using the perturbation expansion for the chemisorption energy.

To illustrate our new diagram technique, we consider briefly the weak-coupling limit. In this limit we write the Green function $\mathcal{L}_{aa\sigma}(z)$ in the form analogous to that of (24):

$$\mathcal{L}_{aa\sigma}(z) = [z - \varepsilon_a - \Sigma_{0wc}(z) - \Delta\Sigma_{wc}(z) - \pi V^2\Lambda(z)]^{-1} \quad (30)$$

where $\Sigma_{0wc}(z)$ is the atomic limit $V \to 0$ of $\Sigma_0(z)$ (19) and for the symmetric case in the strong-coupling regime ($\varepsilon_a < \varepsilon_F$, $\varepsilon_a + U > \varepsilon_F$) is given by $\Sigma_{0wc}(z) = U/2 + M_{0wc}(z)$, $M_{0wc}(z) = U^2/4z$. From (26) in the weak-coupling limit to second order in hybridization for the symmetric case we have

$$\Delta\Sigma^{(2)}_{wc}(z) = U^2[\Gamma(z) + 4m_{wc}(z)]/4z^2 \quad (31)$$

that coincides with the second-order term of equation (16b) of [24]. In (31) we use the notations of [16], namely, $m_{wc}(z) = [\Gamma(z) + \Delta]/2$ where $\Delta = 0$ for the symmetric case. In our notations $\Gamma(z) = \pi V^2\Lambda(z)$. The expression for $\Delta\Sigma^{(2)}_{wc}$ can be also obtained for the asymmetric case.

3. Approximations for the self-energy $\Sigma(z)$

The self-energy is given by $\Sigma(z) = \Sigma_0(z) + \Delta\Sigma(z)$. The Green function $\mathcal{L}_{aa\sigma}$ with $\Delta\Sigma = \Delta\Sigma^{(2)}$ has two extra unphysical poles near the points $z = \pm 3V$ because the function $\Delta\Sigma^{(2)}(z)$ (27) has an extra factor $(z^2 - 9V^2)$ in the denominator in comparison with $M_0(z)$ (19). This extra factor can be eliminated by summation of the set of higher-order terms in the perturbation expansion for $\Delta\Sigma$. Using a simple method, we have that to second order in the rebonding interaction $M_0 + \Delta\Sigma \approx M_0(1 + \Delta\Sigma^{(2)}/M_0)$. Considering the sum $1 + \Delta\Sigma^{(2)}/M_0$ as the starting point of the geometric progression, one obtains that for the symmetric case the self-energy is approximately given by

$$\Sigma_g(z) = U/2 + U^2 z/4[z^2 - 9V^2 - 4\,\Delta\Sigma^{(2)}(z)(z^2 - 9V^2)^2/(U^2 z)]. \tag{32}$$

(32) can be also obtained by an approximate summation of the infinite series of the self-energy electron–hole and the electron–electron ladder diagrams formed from the vertex functions $\Gamma_{2,\sigma\sigma'}$.

In the weak-coupling limit $M_{0wc}(z) = U^2/4z$, $\Delta\Sigma_{wc}^{(2)}$ is given by (31). Then the same approximation for the weak-coupling limit yields

$$\Sigma_{gwc}(z) = U/2 + U^2/4[z - \Gamma(z) - 4m_{wc}(z)]. \tag{33}$$

For the symmetric case the second term in the right-hand side of (33) coincides with (16b) of [24], which follows exactly from (3.10) of [16]. For the Anderson model the function $m(z)$ defined formally by (3.10) of [16] may be considered as a more fundamental object than $\Sigma(z)$. In that approach to second order in the rebonding interaction from (24) and (3.10) of [16] we have $m_{sc}(z) = 9V^2/(4z) - \Gamma(z)/4 + \Delta m_{sc}^{(2)}(z)$ where

$$\Delta m_{sc}^{(2)} = \Delta\Sigma^{(2)}(z)(z^2 - 9V^2)^2/(Uz)^2. \tag{34}$$

Substituting $m_{sc}(z)$ into (33) instead of $m_{wc}(z)$, we obtain (32) again.

The self-energy $\Sigma_g(z)$ (32) is caused by the same transitions as $\Delta\Sigma^{(2)}(z)$. To fourth order in the rebonding interaction the next types of correction to $\Delta\Sigma^{(2)}$ appear: (i) corrections to the numerator of $\Delta\Sigma^{(2)}$, which are neglected in the present paper; (ii) the second-order corrections to the energies $d_{21} + \varepsilon$ and $d_t + \varepsilon$ entering the denominator of $\Delta\Sigma^{(2)}$ which depends strongly on U and have the form $\alpha + x\beta$ for the $|21\rangle$ state and $\alpha - x\beta$ for the triplet states; (iii) the contribution $\Delta\Sigma_4(z)$ to $\Delta\Sigma(z)$ caused by the transitions from the ground state of the doubly occupied SM to the singly or triply occupied states of the SM plus extra electrons or holes in the remaining metal. To sixth order in the rebonding interaction we have the contribution $\Delta\Sigma_6(z)$ caused by transitions from the ground state of the remaining metal to its excited states. The complete calculation of $\Delta\Sigma_4$ and $\Delta\Sigma_6$ is very complicated. We take into account the contributions $\Delta\Sigma_4$ and $\Delta\Sigma_6$ to second order in U and in all orders in $\chi(z)$ by calculating the sum of diagrams which include the vertex functions Γ_4 and Γ_6, and retaining only the terms caused by the transitions discussed. During the calculations we set $\varepsilon_a + U/2 = 0$ and $M_0 = \Delta\Sigma = 0$ in the denominators of the Green functions $G_{ij\sigma}(z)$. As a result, for the symmetric case we have

$$\Delta\Sigma_4(z) = 3U^2 F \int_{-1}^{0} d\varepsilon_1 \int_{-1}^{0} d\varepsilon_2 \left(\frac{\rho_0(\varepsilon_1)\rho_0(\varepsilon_2)}{z - \varepsilon_1 - \varepsilon_2 + |\varepsilon_l|} + \frac{\rho_0(\varepsilon_1)\rho_0(\varepsilon_2)}{z + \varepsilon_1 + \varepsilon_2 - |\varepsilon_l|} \right) \tag{35}$$

$$\Delta\Sigma_6(z) = U^2 \int_{-1}^{0} d\varepsilon_1\, d\varepsilon_2\, d\varepsilon_3\, \rho_0(\varepsilon_1)\rho_0(\varepsilon_2)\rho_0(\varepsilon_3) \left[\frac{1}{z - \varepsilon_1 - \varepsilon_2 - \varepsilon_3} + \frac{1}{z + \varepsilon_1 + \varepsilon_2 + \varepsilon_3} \right] \tag{36}$$

where $\rho_0(\varepsilon)$ is the adatom density of states, ε_l is the energy of the localized state and F is its weight for $U = 0$, $\varepsilon_a = 0$. (35) and (36) can also be extracted from the expression for

$\Sigma(z)$ of [25] obtained to second order in U. Finally, we suggest the next approximation for the self-energy $\Sigma(z)$ near the SM limit:

$$\Sigma(z) = \Sigma_g(z) + \Delta\Sigma_4(z) + \Delta\Sigma_6(z). \tag{37}$$

4. Chemisorption of a one-level atom on a free-atom chain

To check the accuracy of our approximations (32) and (37) for the self-energy, we calculate the adatom density of states and the chemisorption energy for the exactly solvable model of a one-level atom being joined to the end of a chain consisting of three metal atoms [14]. If T is the hopping integral between nearest neighbours in the metal chain, then $\chi(z) = zT^2/(z^2 - T^2)$. For the sake of simplicity we consider below only the symmetric case so that it is sufficient to calculate the quasiparticle levels ε_i and their weights W_i on the adatom only for the positive energies (electrons). We have calculated the parameters α and β, which determine the second-order corrections to the energies $d_{21} - T$ and $d_t - T$, taking into account the dependence of the Fermi energy on the spin projection σ for the adatom-chain system with the odd finite number of electrons $N = 4 \pm 1$.

Table 1. Chemisorption energies E, quasiparticle levels ε_i and their weights W_i on the adatom chemisorbed on a three-atom chain for $V = 5$, $U = 8$ and $T = 1$.

	Exact		Equation (37)		[26]		Equation (32)	
	Level	Weight	Level	Weight	Level	Weight	Level	Weight
i	$E = -7.5395$		$E = -7.5404$		$E = -7.5395$		$E = -7.5396$	
1	0.9783	0.0208	0.9782	0.0208	0.9783	0.0208	0.9783	0.0208
2	2.9346	1.5×10^{-5}	2.9394	1.3×10^{-5}	2.9395	$< 10^{-6}$		
3	4.8996	0.4323	4.8964	0.4318	4.9011	0.4331	4..9005	0.4333
4	6.6926	0.0021	7.0720	0.0022	7.0721	0.0023		
5	9.6989	0.0029	9.4113	0.0039			8.9900	0.0050
6	13.0748	0.0087	12.7846	0.0082	11.2731	0.0082	12.7947	0.0075
7	15.9347	0.0321	15.9176	0.0330	15.8205	0.0356	15.9025	0.0334

Table 2. The same as table 1 for $V = 3$, $U = 8$ and $T = 1$.

	Exact		Equation (37)		[26]		Equation (32)	
	Level	Weight	Level	Weight	Level	Weight	Level	Weight
i	$E = -3.7583$		$E = -3.7719$		$E = -3.7584$		$E = -3.7580$	
1	0.9301	0.0608	0.9292	0.0608	0.9302	0.0608	0.9300	0.0608
2	2.7383	0.0804	2.7748	0.1282	2.7820	0.1089		
3	2.9173	0.2401	2.9094	0.1886	2.9225	0.2148	2.8585	0.3176
4	4.4343	0.0106	5.1260	0.0112	5.1281	0.0120		
5			6.5907	-3.3×10^{-5}			5.1063	0.0227
6	8.8880	0.0538	8.2295	0.0555	7.5658	0.0286	8.6363	0.0453
7	10.5216	0.0401	10.4919	0.0557	10.8135	0.0749	10.4766	0.0536

In tables 1 and 2 we compare our results with the exact ones presented in [17] and the results obtained by the rather accurate method of [26] (these results are also presented in [17]). The method of [26] is based on the interpolation between the expression for $\Sigma(z)$ to

second order in U [25] and the limit of $\Sigma(z)$ for $V \to 0$. From tables 1 and 2 it follows that a rather good agreement with the exact solution is obtained for the approximation (37) for $\Sigma(z)$. In the region of low quasiparticle energies our results are also in good agreement with the results of [17], but in the high-energy region we have obtained a more complex structure for $V = 5$, $U = 8$.

The quasiparticle levels at ε_1, ε_3 and ε_7 exist already in the limit $\Delta\Sigma = 0$ and their interpretation is well known [16, 25]. The levels at ε_2 and ε_4 arise from the poles of $\Delta\Sigma_6(z)$ and $\Delta\Sigma_4(z)$, respectively. The physical nature of these poles was discussed above. Since $d_t - d_{21} = 2x = U/2$, we have obtained two levels at ε_5 and ε_6 instead of the single level of [17] and [26]. These levels correspond to the poles of $\Delta\Sigma^{(2)}(z)$. At the same time, we have calculated the weights W_5 and W_6 only to second order in the rebonding interaction so the inclusion of the higher-order corrections W_2 and W_4 in the approximation (37) disturbs the balance between the energies ε_i and weights W_i because of the constraint $\Sigma_i W_i = 0.5$. For this reason we have obtained better chemisorption energies for approximation (32) than for approximation (37). The chemisorption energy was calculated using the equation of [19].

For $V = 5$ and $U = 8$ the weights W_4 and W_5 have the same order because for the chain model the denominator of the adatom Green function $D(z)$ depends strongly on z. Let γ_i, where $\gamma_4 \sim \chi^2$ and $\gamma_5 \sim \chi$, be small parameters which describe the contributions of the corresponding transitions to the self-energy. Since $W_i \sim 0.5\gamma_i/[\varepsilon_i D^2(\varepsilon_i)]$ and $D^2(\varepsilon_5) \gg D^2(\varepsilon_4)$, one has $W_4 \sim W_5$.

for $V = 3$ and $U = 8$ and the approximation (37) the absolute value of W_5 is very small (the exact solution gives $W_5 = 0$). The negative sign of W_5 indicates that for $U \geqslant 2V$ the perturbation expansion in the rebonding interaction is less applicable than for $U \leqslant 2V$. The interesting fact that for $V = 3$ and $U = 8$ one obtains $W_2 \gg W_4$, $W_2 \sim W_3$ is explained by the resonance between the levels $\varepsilon_3 \approx V = 3$ and $\varepsilon_2 \approx 3T = 3$. For the transition metals having continuous electron density of states the problem of interrelations between the weights W_i is somewhat simpler: the levels ε_2, ε_4, ε_5 and ε_6 spread into continuous bands and the values ρ_i of the adatom density of states within these bands follow on the whole the natural hierarchy ρ_5, $\rho_6 \sim \chi$; $\rho_4 \sim \chi^2$; $\rho_2 \sim \chi^3$.

5. Conclusion

Using the perturbation expansion in the rebonding interaction near the SM limit, we have proposed a new diagram technique for the Anderson model. On the basis of this diagram technique we have obtained an expression for the self-energy to second order in the rebonding interaction and suggested approximate expressions for the self-energy beyond the second order. The potential limitations of the method are connected with the worsening of the accuracy of calculations when the hybridization parameter V decreases or the Coulomb repulsion U increases. To check the accuracy of our method, we have compared the results of our calculations with the exact ones [17] obtained for hydrogen chemisorbed at the end of a chain consisting of three metal atoms. Our results for the quasiparticle spectrum in the case of the finite-chain model are more accurate in the high-energy region than those obtained by the method proposed in [26]. Applications to more realistic models are in progress.

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