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The calculation of the chemisorption energy using the new diagram technique for the Anderson model

I.G. Medvedev[a]

A.N. Frumkin Institute of Electrochemistry of the Russian Academy of Sciences, Leninsky prospect 31, 117071 Moscow, Russia

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Abstract. Using the perturbation expansion in the rebonding interaction near the surface molecule limit, the new diagram technique for the calculation of the chemisorption energy in the Anderson model is proposed. The new expression for the chemisorption energy in the ring diagram approximation is presented. The approximate expression for the contribution of the non- ring diagrams is suggested. The chemisorption energies are calculated and compared with the available exact results and others in the literature. A simple explanation of observable trends in hydrogen chemisorption energies along the transition metal series is given based on the rebonding surface molecule picture.

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1 Introduction

Electron-electron correlations play an important role in adsorption phenomena on transition metals [1]. In particular, they give the contribution to the chemisorption energy and determine essentially the value of the excess adatom charge. In the last decade the first-principle methods of calculations of the hydrogen chemisorption energy have been considerably advanced (see *e.g.* the recent papers [2–6]). These methods use not only the local version of the density functional theory but also take into account the non-local exchange-correlation interactions which permits chemical accuracy to be achieved. However, the performed calculations are complicated and time consuming so that every method is applied to the case of hydrogen chemisorption on a certain transition metal. Therefore, it is difficult to reveal the effect of different physical factors (*e.g.* electron-electron correlations, the parameters of the electronic structure of a metal) on the obtained numbers. Thus, to interpret the results of the *ab initio* calculations and to study the effect of different physical factors on the chemisorption energy and the excess adatom charge it is necessary to consider the more simple models of chemisorption.

This problem was already pointed out in reference [7] where a simple model has been used for the understanding of the results of the first density-functional calculations for hydrogen and lithium chemisorption on free-electron-like substrates. A number of simple calculation schemes has also been elaborated for the case of hydrogen chemisorption on transition metals. Among these are the tight-binding method [8], the embedded cluster method [9], the tight-binding method including the electron correlation contribution in the second order in the Coulomb interaction (see *e.g.* the review paper [10] and references therein) and the effective medium approach [11].

The present paper addresses the same problem and provides a simple explanation of trends in hydrogen chemisorption energies along the transition metal series basing on the rebonded surface molecule point of view within the Anderson-Newns model [12,13] of chemisorption. The Anderson-Newns model does contain many-body effects in an important part – the adatom – and describes the chemical bond between a metal with a continuum of itinerant electron states and an adatom with a discrete localized level.

The Anderson Hamiltonian has the form

$$H = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\sigma} \Big(\varepsilon_a n_{a\sigma} + \frac{1}{2} U n_{a\sigma} n_{a-\sigma} \Big) + \sum_{k,\sigma} \big(V_{ak} c^{+}_{a\sigma} c_{k\sigma} + \text{h.c.} \big) \tag{1}$$

where ε_k and $n_{k\sigma} = c^{+}_{k\sigma} c_{k\sigma}$ are the electronic energies of the metal quasi-particle states $/k\rangle$ and corresponding occupation number operators, ε_a and $n_{a\sigma} = c^{+}_{a\sigma} c_{a\sigma}$ are the energy and occupation number operator of the electronic orbital $/a\rangle$ of an adatom, and σ is the spin projection. The first term in the right-hand side of equation (1)

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[a] e-mail: `theor@serv1.phyche.ac.ru`

describes the metal in the one-particle approximation. The second and the third terms represent the Hamiltonian of an adatom having the single non-degenerate electronic orbital which may be occupied by two electrons with the opposite projection of spins. In particular, the third term takes into account the Coulomb repulsion between these electrons where U is the Coulomb repulsion energy. The last two terms describe the hybridization of the electronic metal states with the electronic orbital of an adatom with V_{ak} as coupling constants. In the present paper the energies of single-particle states are measured relative to the center of the substrate energy band, the energy unit is given by $B/2$ where B is the bandwidth. $V=(\Sigma_k|V_{ak}|^2)^{1/2}$ is the hybridization parameter.

The Anderson-Newns model has three exactly solvable limits when one of the parameters U, V or B is equal to zero [14]. The Anderson model has been solved exactly by the Bethe-Ansatz method in the infinite bandwidth limit, *i.e.* $B \gg U,\ V,\ \varepsilon_a$ [15]. The Anderson model can also be solved exactly in the limiting case when the substrate energy band has only one electron (or hole), and the problem reduces to a two-particle problem [16]. In the general case one needs an approximate treatment of the Anderson-Newns model. The traditional perturbation methods for the Anderson model use the expansion in the hybridization or the Coulomb repulsion [1,10]. However, for the hydrogen chemisorption problem the hopping parameter V, the Coulomb repulsion U and the bandwidth B have the same order of magnitude so that expansions in the hybridization and the Coulomb repulsion as well as a number of decoupling methods are not fully justified procedures. It should be noted that the exact Bethe-Ansatz results for the infinite bandwidth limit can be expanded in power series in a U [17]. At the same time, it is not clear in advance why the second order term in U used in reference [10] will give reasonable results for the correlation energies at finite bandwidth. As shown below, it is the case for the hydrogen chemisorption on the transition metals.

The rebonded surface complex point of view is known to give a reasonable account of the bonding curve near the chemisorption minimum [18,19]. Therefore, in order to study many body effects in adsorption phenomena on transition metals, we have proposed in reference [20,21] the new diagram technique for the Anderson model which is based on the perturbation expansion in the rebonding interaction near the surface molecule (SM) limit. From equation (1) it follows that the adatom level couples directly only with the normalized state

$$|b\rangle = V^{-1}\sum_k V^*_{ak}|k\rangle \tag{2}$$

introduced in [22]. 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 each other. The states $|p\rangle$ are also chosen to be the eigenstates of the remaining metal [21]. Here the term "the remaining metal" designates the metal from which the state $|b\rangle$ is detached. Then the Anderson Hamiltonian (1) can be rewritten in the form [20,21,23,24]

$$H = H_{\rm sm} + \sum_{p,\sigma}\lambda_p c^+_{p\sigma}c_{p\sigma} + \Delta H. \tag{3}$$

Here $H_{\rm sm}$ is the Hamiltonian of the $a-b$ SM

$$\begin{aligned} H_{\rm sm} = \sum_\sigma \Big\{ & \varepsilon_a n_{a\sigma} + \varepsilon_b n_{b\sigma} \\ & + \frac{1}{2}U n_{a\sigma}n_{a-\sigma} + V(c^+_{a\sigma}c_{b\sigma} + \text{h.c.})\Big\}, \end{aligned} \tag{4}$$

$\varepsilon_b = V^{-2}\sum_k \varepsilon_k |V_{ak}|^2$ is the energy of the state $|b\rangle$. The second term in the right-hand side of equation (3) is the Hamiltonian of the remaining metal, $c^+_{p\sigma}$, $c_{p\sigma}$ are the creation and annihilation operators of an electron in the state $|p\rangle$ of the remaining metal with the energy λ_p. ΔH is the rebonding interaction:

$$\Delta H = \sum_{p,\sigma}\left(\frac{\mu_p}{2}c^+_{p\sigma}c_{b\sigma} + \text{h.c.}\right) \tag{5}$$

which describes the rebonding of SM to the remaining metal. The energies λ_p and μ_p are given by equations (11) of reference [21].

We have presented in [20,21] the diagrammatic representation of the adatom Green function and obtained the expression for the self-energy in the second order in the rebonding interaction. The chemisorption energy can be calculated by the substitution of the adatom Green function into the equation of reference [25] for the binding energy. The chemisorption energy can also be calculated directly using the perturbation expansion for the thermodynamic potential (see *e.g.* Ref. [26]) in the limit when the temperature T goes to zero. This method seems to be more appropriate because the perturbation expansion for the thermodynamic potential is organized so perfectly that the summation of the infinite series of the simple ring diagrams gives rather accurate results for the chemisorption energy.

In Section 2 of the present paper we propose the new diagram technique for the calculation of the chemisorption energy of a one-level atom on a transition metal. This technique is analogous to that of reference [21] for the adatom Green function and uses the perturbation expansion of the thermodynamic potential in the rebonding interaction. It should be noted that the same perturbation expansion can be also applied to the magnetic impurity problem in the case when the impurity atom interacts strongly with the narrow band alloy. From the very beginning we consider the limit $T \to 0$. It can be shown that in this limit the change $\Delta\Omega$ of the thermodynamic potential due to the rebonding interaction ΔH of SM with the remaining metal goes to the corresponding change ΔE of the chemisorption energy.

We write the total chemisorption energy E of a one-level atom on a transition metal in the form [27]

$$E = \Delta E_{20} + E_b + \Delta E \tag{6}$$

where ΔE_{20} is the bonding energy of the doubly-occupied SM in the singlet state, E_b is the energy of the separation of the singly-occupied state $|b\rangle$ from the metal, and ΔE is the exact energy of the rebonding of SM to the remaining metal. Equation (1) with $\Delta E = \Delta E^{(2)}$, where $\Delta E^{(2)}$ is the energy of the interaction of SM with the remaining metal up to the second order in the rebonding interaction, has already been used in references [18,19,23,24] for different models of the chemisorption process. For the asymmetric Anderson model and the arbitrary electronic density of states of a metal the energies ΔE_{20} and E_b have been defined and studied in [28]. The expression for E_b for the general case is obtained below.

Using the perturbation expansion in the rebonding interaction, we have suggested in [27] the ring diagram approximation (RDA) for ΔE which is exact in a number of important limiting cases, simple and yet accurate-enough for the calculations of the energies of hydrogen chemisorption on transition metals. On the basis of this approximation the role of the electron correlation effects in adsorption phenomena on transition metals has been studied [29]. In Section 3 the new simple expression for the chemisorption energy in RDA is presented. This expression elucidates the physical meaning of RDA and permits the simple calculations of the chemisorption energies and the excess adatom charge.

Thus, the diagram technique suggested in the present paper provides the foundation of the simple and transparent physical picture of hydrogen chemisorption on transition metals. This picture is given by expression (6) and consists in the formation of SM and its subsequent interaction with the remaining metal.

The non-ring diagrams include the vertex functions Γ_k introduced in references [20,21]. We present in Section 3 the expression for the contribution $\Delta E_{\mathrm{nr}}^{(4)}$ of the non-ring diagram of the fourth order in the rebonding interaction for the symmetric case. The approximate expression for the contribution δE_{nr} of the non-ring diagrams, which includes the terms beyond the fourth order, is suggested in Section 4. This expression is based on the summation of the infinite class of the non-ring diagrams which have as a skeleton the non-ring diagram of the fourth order. Using the considered approximations, the chemisorption energies are calculated for different models of substrate and compared with the available exact results and others in the literature. It is shown that RDA is very accurate for $V > U/4$. Taking into account the contribution δE_{nr}, one can calculate properly the chemisorption energy for the lower values of V.

Finally, in Section 5, we present the results of calculations of hydrogen chemisorption energies on the $5d$-transition metal surfaces at the equilibrium position of an adatom. It is shown that the obtained trends in hydrogen chemisorption energy are in agreement with experiment. The simple explanation of these trends is given in terms of the energies ΔE_{20}, E_b and ΔE.

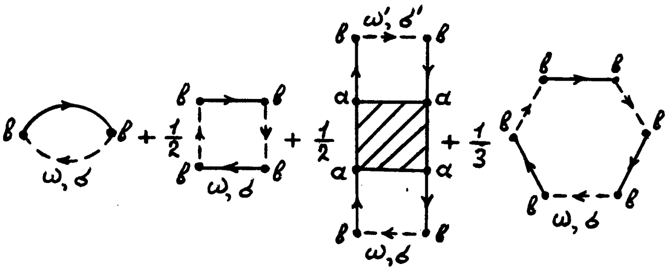

Fig. 1. Diagrammatic representation for the energy of the rebonding interaction ΔE.

2 The diagram technique for the chemisorption energy

The interaction energy of SM with the remaining metal is given by

$$\Delta E = -\lim_{T\to 0} \frac{1}{\beta} \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \times \int_0^\beta \mathrm{d}\tau_1 ... \int_0^\beta \mathrm{d}\tau_n \langle T \Delta H(\tau_1) ... \Delta H(\tau_n)\rangle_{\mathrm{c}} \quad (7)$$

where $\beta = (kT)^{-1}$, $\Delta H(\tau) = \exp(\tau H')\Delta H \exp(-\tau H')$, $H' = H - \Delta H - \mu N$, H is the Anderson Hamiltonian, N is the total number of electrons in the system, μ is the chemical potential which in the case of a metal having macroscopic volume goes to the Fermi energy ε_{F} when $T \to 0$.

ΔE is equal to the sum of the contributions of the connected diagrams which are constructed as for the adatom Green function [21]. The diagrams for ΔE which do not include the vertex functions Γ_k, we have called the ring diagrams [27]. Let $\Delta E_{\mathrm{r}}^{(n)}$ and $\Delta E_{\mathrm{nr}}^{(n)}$ be the ring and non-ring diagram contribution to the chemisorption energy in the n order in the rebonding interaction, so that $\Delta E^{(n)} = \Delta E_{\mathrm{r}}^{(n)} + \Delta E_{\mathrm{nr}}^{(n)}$ for $n > 2$ because $\Delta E^{(2)} = \Delta E_{\mathrm{r}}^{(2)}$. These diagrams up to the fourth order in the rebonding interaction are shown in Figure 1. In Figure 1 we also present the ring diagram of the sixth order. Heavy lines depict the temperature Green functions $G_{ij\sigma}(z)$ of the non-perturbed SM in the limit $T \to 0$. Here $i, j = a, b$, $z = \varepsilon_{\mathrm{F}} + \mathrm{i}\omega$ and the Fourier transform of $G_{ij\sigma}(\tau)$ is defined by equation

$$G_{ij\sigma}(\tau) = \frac{1}{\beta} \sum_n G_{ij\sigma}(\mu + \mathrm{i}\omega_n) \exp(-\mathrm{i}\omega_n \tau), \quad \omega_n = (2n+1)\pi/\beta. \quad (8)$$

The ends of heavy lines are marked by the indices i and j. A dashed line corresponds to the function $\chi(z)$ [21]. This function describes the effective contribution of electrons propagating in states $|p\rangle$ to the interaction of SM with the remaining metal. The lined square depicts the vertex function $\Gamma_{2;\sigma\sigma'}(z, z', z')$ which includes the lines of the electron-electron interaction and is given by equation (20) of [21]. The summation over the spin indices and integration over the independent energies ω, ω' is performed.

Functions $G_{ab}(z)$, $G_{ba}(z)$ and $G_{bb}(z)$ are expressed through $G_{aa\sigma}(z)$ [21]. For the Green functions $G_{aa\sigma}(z)$ and $G_{ab\sigma}(z)$ in the general asymmetric case we have

$$\begin{aligned} G_{aa\sigma}(z) &= [z - \varepsilon_a - \Sigma_0(z) - \pi V^2 \Lambda_0(z)]^{-1}, \\ G_{ab\sigma}(z) &= G_{ab\sigma}(z) = V G_{aa\sigma}(z)/(z - \varepsilon_b), \end{aligned} \tag{9}$$

where $\Lambda_0(z) = [\pi(z - \varepsilon_b)]^{-1}$ and $\Sigma_0(z)$ is the self-energy:

$$\begin{aligned} \Sigma_0(z) &= U n_{a0}/2 + M_0(z); \\ M_0(z) &= \frac{Dz + c}{z^2 - (t - U\Delta n_{a0}/2)z - B}\cdot \end{aligned} \tag{10}$$

Here $t = \varepsilon_a + U/2$, n_{a0} is the average number of electrons on an adatom in the SM limit and $\Delta n_{a0} = n_{a0} - 1$ is the excess adatom charge. Using the results of reference [30] for $M_0(z)$, we obtain that

$$D = U^2(1 - \Delta n_{a0}^2)/4;$$

$$C = \Delta E_{20} U[\Delta n_{a0}(\Delta E_{20} - U/2) - t]; \tag{11}$$

$$B = 2\Delta E_{20}(\Delta E_{20} - U/2) + V^2; \tag{12}$$

$$\Delta n_{a0} = \frac{2t\Delta E_{20}}{3\Delta E_{20}^2 - 2U\Delta E_{20} - t^2 - 4V^2 + U^2/4}; \tag{13}$$

$$\Delta E_{20} = -2\left(-\frac{p}{3}\right)^{1/2} \sin\left[\frac{\pi + \mathrm{arctg}(0.5q/D^{1/2})}{3}\right] + U/3; \tag{14}$$

where $p = -(t^2 + 4V^2 + U^2/12)$, $q = U(p + 6V^2 + U^2/9)/3$, $D = -(q/2)^2 - (p/3)^3$ and $D > 0$ for $V \neq 0$.

Below we also use the next form of the Green function $G_{bb\sigma}(z)$ [27]:

$$G_{bb}(z) = \sum_{\alpha}\left(\frac{\kappa_{1\alpha}}{z - d_{1\alpha}} + \frac{\kappa_{3\alpha}}{z + d_{3\alpha}}\right) \tag{15}$$

where $\kappa_{1\alpha} = |\langle 20|c^{+}_{b-\sigma}|1\alpha\sigma\rangle|^2$, $\kappa_{3\alpha} = |\langle 20|c_{b\sigma}|3\alpha\sigma\rangle|^2$, $d_{i\alpha} = \Delta E_{20} - \Delta E_{i\alpha}$ and $d_{i\alpha} < 0$ for all values of ε_a, $\Delta E_{1\alpha} = E_{1\alpha} - \varepsilon_a$, $\Delta E_{3\alpha} = E_{3\alpha} - 2\varepsilon_b - \varepsilon_a$, $|i\alpha\sigma\rangle$ and $E_{i\alpha}$ are the state and the energy of SM having $i = 1, 3$ electrons, $\alpha = \pm$ and the index "–" labels the state $|i\rangle$ with the lowest energy.

Let $\Delta(\varepsilon)$ be the electronic density of states of the substrate projected into the orbital $|b\rangle$ and $\Lambda(\varepsilon)$ be its Hilbert transform. Then from references [20,21]

$$\chi(z) = z - \varepsilon_b - [\pi\Lambda(z)]^{-1} \tag{16}$$

where $\Lambda(z)$ is the analytic continuation of $\Lambda(\varepsilon)$ from the interval $(1, \infty)$ of the real axis into the complex plane with the cut [-1,1].

3 The ring diagram approximation

From Figure 1 it follows that the factor at the given ring diagram of the nth order in the rebonding interaction is equal to $1/k$, where $k = n/2$ and coincides with the order in $\chi(z)$. Therefore, the series consisting of the contributions of the ring diagrams forms the expression for the logarithmic function. The sum ΔE_{r} of this series we call the interaction energy of SM with the remaining metal in RDA [27]:

$$\Delta E_{\mathrm{r}} = \frac{\mathrm{i}}{\pi}\int \ln[1 - \chi(z)G_{bb\sigma}(z)]\mathrm{d}z \tag{17}$$

where the integration is performed over the line l: $\mathrm{Re}\, z = \varepsilon_{\mathrm{F}}$ in the complex plane with the cut [-1,1] and Im(ln) is taken from $-\pi$ to π. For, *e.g.*, the semi-elliptic density of states $\Delta(\varepsilon)$ we have $\chi(z) = [z - (z^2 - 1)^{1/2}]/2$ and in the symmetric case

$$\Delta E_{\mathrm{r}} = -\frac{2}{\pi} \times \int_0^{\infty} \mathrm{d}\,\omega\, \ln\left\{1 + \frac{\omega[(\omega^2 + 1)^{1/2} - \omega](\omega^2 + 4x^2 + 9V^2)}{2[\omega^4 + 2(2x^2 + 5V^2)\omega^2 + 9V^4]}\right\} \tag{18}$$

where $x = U/4$. The energy ΔE_{r} (18) as well as the energy ΔE_{r} (17) for $\varepsilon_{\mathrm{F}} = 0$ and arbitrary ε_a are the analytic functions of V in the vicinity of the real axis for $V > 0$. Thus, although the perturbation expansion in the rebonding interaction is formally valid for $V > 1$, the functions $\Delta E_{\mathrm{r}}(V)$ (17-18) can be analytically continued to the region of small V and give the exact energy ΔE in the limit $U \to 0$ because in this limit $\Gamma_k \equiv 0$. As follows from equation (15), in the asymmetric case for $\varepsilon_{\mathrm{F}} \neq 0$ expression (17) for ΔE_{r} is valid for $d_{3-} < -(\varepsilon_{\mathrm{F}} - \varepsilon_b)$ and $d_{1-} < \varepsilon_{\mathrm{F}} - \varepsilon_b$.

The chemisorption energy E_{r} in RDA is given by [27]

$$E_{\mathrm{r}} = \Delta E_{20} + E_b + \Delta E_{\mathrm{r}}. \tag{19}$$

For the symmetric case the energy E_b has been obtained in reference [24]. In the general case the energy of the separation of the singly-occupied state $|b\rangle$ from the metal is defined as

$$E_b = \varepsilon_b + \sum_{p,\sigma} f(\lambda_p)\lambda_p - \sum_{k,\sigma} f(\varepsilon_k)\varepsilon_k \tag{20}$$

where $f(x)$ is the Fermi function. The energies λ_p are the zeroes of the function $\widetilde{\Lambda}(z) = (\pi V^2)^{-1}\sum_k |V_{ak}|^2/(z - \varepsilon_k)$ [21] and the energies ε_k are its poles. In the macroscopic limit the function $\widetilde{\Lambda}(z)$ goes to $\Lambda(z)$. Let N_k and N_p be the total numbers of electrons in the metal and in the remaining metal, respectively. Since $N_k = N_p + 1$, we have

$$E_b = \varepsilon_b + \frac{1}{2\pi\mathrm{i}}\oint_{\lambda} z\frac{\mathrm{d}\ln\widetilde{\Lambda}(z)}{\mathrm{d}z}\mathrm{d}z - \varepsilon_{\mathrm{F}} \tag{21}$$

where the contour λ encloses all the points λ_p and ε_k with the exception of ε_{F}, and the transition from the summation over p and k to the integration is analogous to that used in reference [13] for the calculation of the chemisorption energy. Finally, in the macroscopic limit one obtains

$$E_b(\varepsilon_{\mathrm{F}}) = -\frac{2}{\pi}\int_{-1}^{\varepsilon_{\mathrm{F}}} \mathrm{arctg}\left[\frac{\Delta(\varepsilon)}{\Lambda(\varepsilon)}\right]\mathrm{d}\varepsilon + \varepsilon_b - \varepsilon_{\mathrm{F}}. \tag{22}$$

Here arctg is taken from $-\pi$ to 0 so that for $\varepsilon_{\mathrm{F}} = \pm 1$ the energy $E_b = 1$, as follows directly from its physical meaning, and for the symmetric function $\varDelta(\varepsilon)$ one has $E_b(\varepsilon_{\mathrm{F}}) = E_b(-\varepsilon_{\mathrm{F}})$. The dependence of the energy $E_b(\varepsilon_{\mathrm{F}})$ on the density of states $\varDelta(\varepsilon)$ is studied in the Appendix.

Let $M_1 < 0$ and $M_2 > 0$ be the poles of $M_0(z)$ (10). If in equation (17) we go from the integration over the line λ to the integration over the banks of the cut [–1,1] and use equation (22) for E_b, we obtain that for $|M_1|$,$M_2 > 1$

$$E_{\mathrm{r}} = 2(\varepsilon_{12} - \varepsilon_b - d_{1+}) + 2(\varepsilon_{l1} + 1) + \varepsilon_{\mathrm{F}} - \varepsilon_a - \{\varDelta E_{20} - 2\varDelta E_{1-} - \varepsilon_a + \varepsilon_b\} + \frac{2}{\pi} \times \int_{-1}^{\varepsilon_{\mathrm{F}}} \mathrm{arctg}\left[\frac{\pi V^2 \varDelta(\varepsilon)}{\varepsilon - \varepsilon_a - U n_{a0}/2 - M_0(\varepsilon) - \pi V^2 \varLambda(\varepsilon)}\right] \mathrm{d}\varepsilon. \tag{23}$$

Here arctg is taken from $-\pi$ to 0, ε_{l1} and ε_{l2} are the roots of the function $\varepsilon - \varepsilon_a - U n_{a0}/2 - M_0(\varepsilon) - \pi V^2 \varLambda(\varepsilon)$ in the region $\varepsilon < -1$. This function coincides with the denominator of the adatom Green function $\widetilde{L}_{aa\sigma}(z)$ [20] which corresponds to the approximation $\sum(z) = \sum_0(z)$. Thus, the energies ε_{l1} and ε_{l2}, where $\varepsilon_{l2} \leq M_1 < \varepsilon_{l1} \leq -1$, are the energies of the localized states in the case when $\sum(z) = \sum_0(z)$. If the localized state ε_{l1} is absent, the term $(\varepsilon_{l1} + 1)$ in equation (23) should be omitted. Since $|M_1|$, M_2 have the order of 3 V, the condition $V > B/6$ always takes place for the hydrogen chemisorption on transition metals. However, it may happen for large values of ε_a that $M_1 > -1$. The identity $E(\varepsilon_a, \varepsilon_{\mathrm{F}}) = E(-(\varepsilon_a + U), -\varepsilon_{\mathrm{F}})$ can be used in this case.

RDA is exact in the second order in the rebonding interaction because $\varDelta E^{(2)} = \varDelta E_{\mathrm{r}}^{(2)}$. For $U = 0$ we have $M_0(\varepsilon) = 0$. In this limit equation (23) is valid for arbitrary values of ε_a, ε_{F}, and coincides with the exact chemisorption energy of reference [13] for the non-interacting electrons because the first term in (23) and the term in figure brackets equal zero. Thus, RDA in the form (23) is also valid in the limit $U = 0$ for arbitrary ε_{F}.

It should be noted that RDA is not exact in the second order in U because the vertex functions $\varGamma_2$, $\varGamma_3$ and $\varGamma_4$ have an order of U^2 when $U \to 0$. However, as discussed below, the omitted terms have an order of $(U/4V)^2$, the high order in the rebonding interaction, and are therefore small for parameters imitating hydrogen chemisorption on transition metals.

Equation (23) also presents in the explicit form the physical meaning of RDA as the approximation of the dressed non-interacting quasi-particles. For $U \neq 0$ the first term on the right-hand side of equation (23) has the form $2\varepsilon_{l2} W_2$ and is equal to the contribution of the localized state l_2 with the weight W_2 to the chemisorption energy where $W_2 = (\varepsilon_{l2} - \varepsilon_b - d_{1+})/\varepsilon_{l2}$. For the localized state l_1 the weight $W_1 = 1$. The term in figure brackets is equal to $E_{20} - 2E_{1-}$ where E_{20} is the energy of the ground state of the doubly-occupied SM. Since the difference $E_{20} - 2E_{1-}$ coincides with the contribution of the Coulomb interaction to E_{20}, the term in figure brackets eliminates the excess Coulomb interaction energy entering the term $2\varepsilon_{l1}$. In the SM limit $\varepsilon_{l2} = d_{1+} + \varepsilon_b$, $\varepsilon_{l1} = d_{1-} + \varepsilon_b$ and $E_{\mathrm{r}} = \varDelta E_{20}$. The last term in equation (23) gives the contribution of quasi-particles having a continuous energy spectrum.

If we, following [31], substitute the Green function $\widetilde{L}_{aa\sigma}(z)$ with $\varDelta\varSigma(z) = \varSigma(z) - \varSigma_0(z) = 0$ into the equation of reference [25] for the binding energy, we do not obtain the exact second order term in the rebonding interaction because in this case the second order contribution $\varDelta\varSigma^{(2)}$ to the self-energy is omitted. It should be also noted that the method of reference [31] involves the Anderson Hamiltonian with the energy dependent effective parameter ε_a, which can not be considered as a regular procedure. Since the expression for $\varDelta\varSigma^{(2)}$ is very complicated for the asymmetric Anderson model, the simplest way of calculating the chemisorption energy near the SM limit is the perturbation expansion in the rebonding interaction used in the present paper.

From equation (23) we can readily obtain the expression for the excess adatom charge $\varDelta n_{\mathrm{r}}$ in RDA defined as [30]

$$\varDelta n_{\mathrm{r}} = \partial E_{\mathrm{r}}/\partial \varepsilon_a = \varDelta n_{a0} + \varDelta n_{\chi}. \tag{24}$$

Here $\varDelta n_{\chi} = \partial \varDelta E_{\mathrm{r}}/\partial \varepsilon_a$. $\varDelta n_{\mathrm{r}}$ is expressed through $\varDelta n_{a0} = \partial \varDelta E_{20}/\partial \varepsilon_a$, $\chi_{c0} = -\partial \varDelta n_{a0}/\varDelta \varepsilon_a$ where the charge susceptibility χ_{c0} in the SM limit is given by equation (8) of [29]. In the second order in the rebonding interaction we have

$$\varDelta n_{\chi}^{(2)} = \partial \varDelta E^{(2)}/\partial \varepsilon_a = -\frac{\mathrm{i}}{\pi}\int_l \chi(z) \partial G_{bb}(z)/\partial \varepsilon_a \mathrm{d}z \tag{25}$$

where the integration is performed over the line l: Re$z = \varepsilon_{\mathrm{F}}$. At the same time $\varDelta n_{\chi}^{(2)}$ can be calculated using two second order diagrams of Figure 1 of reference [21] for the adatom Green function. On the other hand, from equation (17)

$$\varDelta n_{\chi} = -\frac{\mathrm{i}}{\pi}\int_l \chi_{\mathrm{eff}}(z)\, \partial G_{bb}(z)/\partial \varepsilon_a \mathrm{d}z \tag{26}$$

where $\chi_{\mathrm{eff}}(z) = \chi(z)/[1 - \chi(z) G_{bb}(z)]$. Thus, from equations (25) and (26) it follows that $\varDelta n_{\chi}$ can be also derived from the sum of the two infinite classes of the diagrams for the adatom Green function which are based on the second order diagrams of reference [21], and correspond to the substitution of $\chi_{\mathrm{eff}}(z) = \chi(z) + \chi(z) G_{bb}(z) \chi(z) + ...$ for $\chi(z)$.

To evaluate the accuracy of RDA, we compare the values of E_{r} and $\varDelta n_{\mathrm{r}}$ with the exact ones obtained in the limit of the almost filled substrate energy band [16] for the parameters given by Newns [13] for the case of hydrogen chemisorbed on Ni but for $\varepsilon_{\mathrm{F}} = B/2$: $V = 3.75$ eV, $U = 12.9$ eV, $\varepsilon_a = -8.04$ eV, $B = 3.8$ eV. We have the exact values $E_{\mathrm{exact}} = -3.435$ eV, $\varDelta n_{\mathrm{exact}} = 0.117$ and $E_{\mathrm{r}} = -3.455$ eV, $\varDelta n_{\mathrm{r}} = 0.120$. In this case the dimensionless parameters d_{1-} and d_{3-} are equal to -1.857 and -1.562, respectively. The corresponding contributions to $\varDelta E$ are $\varDelta E^{(2)} = -0.367$ eV, $\varDelta E_{\mathrm{r}}^{(4)} = 0.021$ eV, $\varDelta E_{\mathrm{nr}}^{(4)} = 0.028$ eV so that the sum E$_{\mathrm{r}}$ + $\varDelta E_{\mathrm{nr}}^{(4)}$ equals

-3.427 eV and is close to $E_{\rm exact}$. On the other hand, in the Hartry-Fock approximation $E_{\rm HF} = -2.772$ eV, $\Delta n_{\rm HF} = 0.155$ and the correlation energy equals 0.663 eV.

Equation (23) gives in an explicit form the analytical continuation of $E_{\rm r}(V)$ (17) from the region $V > 1$ to the region $V > 1/3$ for the asymmetric case, and has no discontinuities for $|d_{3-}| = \varepsilon_{\rm F}$ and $d_{1-} = \varepsilon_{\rm F}$. However, when V decreases and *e.g.* $|d_{3-}|$ approaches $\varepsilon_{\rm F} > 0$, the comparison with the exact results for $\varepsilon_{\rm F} = B/2$ shows that the error of RDA reaches 6%. When V further decreases and $|d_{3-}|$ becomes smaller than $\varepsilon_{\rm F}$, the agreement between E and $E_{\rm r}$ worsens abruptly.

On the contrary, when $|d_{3-}|$ decreases due to the decrease of ε_a, RDA works well even for $|d_{3-}| < \varepsilon_{\rm F}$, $|d_{3-}| \to 0$, and is exact in the weak-correlation regime ($\varepsilon_a + U < \varepsilon_{\rm F}$ or $\varepsilon_a > \varepsilon_{\rm F}$) up to the first order in $|\varepsilon_a|^{-1}$ for $|\varepsilon_a| \to \infty$. In this case the condition $|M_1|$, $M_2 > 1$ is conserved. If in the example considered above we take $\varepsilon_a = -20.9$ eV, then $E_{\rm exact} = -10.155$ eV, $\Delta n_{\rm exact} = 0.880$ and $E_{\rm r} = -10.196$ eV, $\Delta n_{\rm r} = 0.881$ for $d_{3-} = -0.708$. In the weak-correlation regime for $\varepsilon_a + U < 0$ or $\varepsilon_a > 0$, RDA is also exact up to the second order in V. These properties of RDA in the weak-correlation regime follow from the behavior of the effective parameter $\gamma(z) = G_{ab}(z)\chi(z)G_{ba}(z)$ of the perturbation expansion of the adatom Green function in the rebonding interaction, which in the weak-correlation regime for $\varepsilon_a + U < 0$ or $\varepsilon_a > 0$ is proportional to V^2 and ε_a^{-2} for $V \to 0$ and $|\varepsilon_a| \to \infty$, respectively. Thus, $\Delta n_{\rm r}$ is exact up to the second order in $|\varepsilon_a|^{-1}$ in the weak-correlation regime and $E_{\rm r} \sim \int \Delta n_{\rm r} {\rm d}\varepsilon_a$ is therefore exact up to the first order in $|\varepsilon_a|^{-1}$. Thus, for parameters V and U imitating hydrogen chemisorption on transition metals, RDA gives smooth interpolation between the strong- correlation and weak-correlation regimes and permits rather accurate calculations to be performed in the intermediate-valence regime when ε_a decreases from $-U/2$ to $-\infty$. However, in the weak-correlation regime the chemisorption energy and the excess adatom charge can be calculated using the Hartree-Fock approximation.

More generally, RDA is valid when $|\Delta E^{(4)}_{\rm nr}| \ll |\Delta E^{(4)}_{\rm r}|$. From the comparison of the diagrammatic representations of the adatom Green function [21] and the chemisorption energy (Fig. 1) it follows that

$$\Delta E^{(4)}_{\rm nr} = -\frac{\rm i}{2\pi}\int_l G_{ab}(z)\chi(z)G_{ba}(z)\Delta\Sigma^{(2)}(z){\rm d}z. \tag{27}$$

We consider only the symmetric case which for $U \neq 0$ corresponds to the strong-correlation regime ($\varepsilon_a < \varepsilon_{\rm F}$ and $\varepsilon_a + U > \varepsilon_{\rm F}$). Then $\Delta\Sigma^{(2)}(z)$ is given by equation (27) of [21] and one obtains

$$\Delta E^{(4)}_{\rm nr} = -\frac{3x^2V^2}{2\pi^2r^2}\int_{-1}^{0}{\rm d}\omega\int_{-1}^{0}{\rm d}\varepsilon \frac{f(t,y)\varphi(\omega)\varphi(\varepsilon)}{[(\varepsilon+d_-)(\varepsilon+d_+)(\omega+d_-)(\omega+d_+)]^2[(\omega+\varepsilon-r)^2-x^2]}. \tag{28}$$

Here $x = U/4$, $r = (x^2+4V^2)^{1/2}$, $t = \varepsilon - r$, $y = \omega - r$, $d_- = d_{3-} = d_{1-}$, $d_+ = d_{3+} = d_{1+}$, $d_\pm = -(r \pm s)$, $s = (x^2+V^2)^{1/2}$, $\varphi(\varepsilon) = -{\rm Im}\chi(\varepsilon + {\rm i}0) = {\rm Im}[\pi\Lambda(\varepsilon+{\rm i}0)]^{-1}$ and

$$\begin{aligned} f(t,y) &= t^2y^2(t^2+y^2) + 2t^3y^3 - 2rty(t^3+y^3) \\ &-4rt^2y^2(t+y) + (x^2+7V^2)(t^4+y^4) + 2(x^2+7V^2)ty(t^2+y^2) \\ &+ 2(x^2+9V^2)t^2y^2 + 4(x^2-V^2)rty(t+y) \\ &- (3x^2+19V^2)s^2(t^2+y^2) - 2(3x^2+15V^2)s^2ty \\ &+ 2(x^2+5V^2)s^2r(t+y) + 4s^4V^2. \end{aligned} \tag{29}$$

The calculation of $\Delta E^{(4)}_{\rm r}$ is straightforward. For the semi-elliptic function $\Delta(\varepsilon)$ in the second order in U we get

$$|\Delta E^{(4)}_{\rm nr}/\Delta E^{(4)}_{\rm r}| = \xi(V)(U/4V)^2 \tag{30}$$

where the function $\xi(V) \approx 0.5$ for $V < 1$. Thus, in the region $V < 1$, RDA is rather accurate for $V > U/4$. In the case $V \geq 1$, both $\Delta E^{(4)}_{\rm r}$ and $\Delta E^{(4)}_{\rm nr}$ are very small as compared with ΔE_{20} and $\Delta E^{(2)}_{\rm r}$, even if $U \sim 4V$ as has been shown above for hydrogen chemisorption on Ni for the parameters given by Newns. In this case we may take into account only the second order term in the rebonding interaction $\Delta E^{(2)}_{\rm r}$. However, it is worthwhile using RDA also in this case because equation (23) is more simple for calculations and has a clear physical meaning.

The energy U of the Coulomb repulsion enters the expressions for the Greens functions and vertex functions through the parameter $x = U/4$ (see *e.g.* Eq. (28)). Since the parameter $s = (x^2+V^2)^{1/2}$ as well as the parameter r can be expanded in powers of $(U/4V)^2$, we obtain from our diagram method that the chemisorption energy can be also expanded in powers of $(U/4V)^2$ at least in the region of V where the perturbation expansion in the rebonding interaction converges. This region of V is evaluated by equation (35) presented in Section 4. Thus, we have obtained the effective parameter of the perturbation expansion of the chemisorption energy in powers of U. The similar parameter $U/\pi\Delta$ emerged in the infinite bandwidth limit [17]. In many chemisorption problems on transition metals $U/4V < 1$ at the equilibrium position, so that the second order perturbation in U should yield a reasonable approximation to the correlation energy which is in accordance with the results of reference [10]. However, at larger distances of adsorbate species from a metal the condition $U/4V < 1$ is violated.

Consider *e.g.* the set of parameters suggested in reference [32] and imitating hydrogen chemisorption on W : $B = 10$ eV, $U = 7.5$ eV, $\varepsilon_a = -U/2$ and $\varepsilon_{\rm F} = 0$. Using the rather accurate method of reference [33], it has been obtained in [32] that the hydrogen chemisorption energy $E = -3.2$ eV for $V = 3.44$ eV, and $E = -2.7$ eV for $V = 3.12$ eV and the semi-elliptic density of states. The method of [33] is based on the interpolation between the expression for the self-energy $\Sigma(z)$ to second order in U [34] and the limit of $\Sigma(z)$ for $V \to 0$. On the other hand, using

$$
\begin{aligned}
\delta E_{\mathrm{nr}} &= 2\left(\frac{-\mathrm{i}}{2\pi}\right)^{2}\sum_{\sigma,\sigma'}\int_{l}\mathrm{d}z\int_{l'}\mathrm{d}z'\int_{0}^{1}\frac{\mathrm{d}\lambda}{\lambda}g(\lambda,z)\Gamma_{2;\sigma\sigma'}(z,z',z')g(\lambda,z')\\
&= \frac{1}{4\pi^{2}}\sum_{\sigma,\sigma'}\int_{l}\mathrm{d}z\int_{l'}\mathrm{d}z'\frac{G_{ab}(z)\chi(z)G_{ba}(z)\Gamma_{2;\sigma\sigma'}(z,z',z')G_{ab}(z')\chi(z')G_{ba}(z')}{\chi(z)G_{bb}(z)-\chi(z')G_{bb}(z')}\\
&\quad\times\left\{\frac{\ln[1-\chi(z)G_{bb}(z)]}{\chi(z)G_{bb}(z)}-\frac{\ln[1-\chi(z')G_{bb}(z')]}{\chi(z')G_{bb}(z')]}\right\}
\end{aligned}
\tag{31}
$$

---

our diagram method, we have $E_{\mathrm{r}} = -3.243$ eV, $\Delta E_{\mathrm{r}}^{(2)} = -1.237$ eV, $\Delta E_{\mathrm{r}}^{(4)} = 0.073$ eV, $\Delta E_{\mathrm{nr}}^{(4)} = -0.011$ eV, $E = E_{\mathrm{r}} + \Delta E_{\mathrm{nr}}^{(4)} = -3.25$ eV for $V = 3.44$ eV and $E_{\mathrm{r}} = -2.708$ eV, $\Delta E_{\mathrm{r}}^{(2)} = -1.332$ eV, $\Delta E_{\mathrm{r}}^{(4)} = 0.108$ eV, $\Delta E_{\mathrm{nr}}^{(4)} = -0.016$ eV, $E = E_{\mathrm{r}} + \Delta E_{\mathrm{nr}}^{(4)} = -2.724$ eV. Thus, the sum $E = E_{\mathrm{r}} + \Delta E_{\mathrm{nr}}^{(4)}$ gives the chemisorption energy with an accuracy up to 0.01 eV. Our results for the chemisorption energy are in excellent agreement with those of [32]. The relation between $\Delta E_{\mathrm{nr}}^{(4)}$ and $\Delta E_{\mathrm{r}}^{(4)}$ agrees in the whole with that given by equation (30). At the same time $E_{\mathrm{HF}} = -2.953$ eV, $\varepsilon_{\mathrm{c}} = E_{\mathrm{HF}} - E = 0.3$ eV, and $E_{\mathrm{HF}} = -2.383$ eV, $\varepsilon_{\mathrm{c}} = 0.34$ eV, for $V = 3.44$ eV and $V = 3.12$ eV, respectively. Other examples are presented in Section 4.

4 The approximation for the calculation of the contribution of the non-ring diagrams to the chemisorption energy

In this section we obtain the approximate expression for the contribution δE_{nr} of the non-ring diagrams to the chemisorption energy which is exact in the fourth order in the rebonding interaction. Namely, we sum the infinite class of the non-ring diagrams having only a single vertex function Γ_2. To eliminate the factor $1/n$ at the diagram of the n-th order, we use the method of the coupling constant λ [26]: the energy μ_p is multiplied by a constant λ (or the function $\chi(z)$ is multiplied by λ^2), the series is summed, the result is divided by λ and integrated with respect to λ from 0 to 1. We obtain that

see equation (31) above

where $g(\lambda, z) = G_{ab}(z)\lambda^2\chi(z)G_{ba}(z)/[1 - \lambda^2\chi(z)G_{bb}(z)]$. For the adatom Green function the analogous procedure gives the self-energy which can be shown [20] to be proportional to V^2 for small values of V. In the considered case the sum $E_{\mathrm{r}} + \delta E_{\mathrm{nr}}$ is not proportional to V^2 in the weak-coupling region due to the additional integration with respect to λ and z. Nevertheless, the correction δE_{nr} to E_{r} permits us to calculate properly the chemisorption energy up to rather small values of V because as discussed below the sum $E(v) = E_{\mathrm{r}}(V) + \delta E_{\mathrm{nr}}(V)$ interpolates approximately between the strong-coupling and weak-coupling limits.

Table 1. The chemisorption energies E_{r}, $E = E_{\mathrm{r}} + \delta E_{\mathrm{nr}}$, the exact chemisorption energies E_{exact} and the energies E_{v} of reference [6] for the finite chain model of adsorption. $U = 2.5$, $\varepsilon_a = -U/2$ and $2T = 1$.

V	$-E_{\mathrm{r}}$	$-E$	$-E_{\mathrm{exac}}$	$-E_{\mathrm{v}}$
0.15	0.03795	0.04215	0.0412	0.04121
0.25	0.10670	0.11290	0.1119	0.11188
0.375	0.23582	0.24138	0.2410	0.24077
0.5	0.40023	0.40415	0.4041	0.40380
1.0	1.22582	1.22656	1.2266	1.22649
1.5	2.15129	2.15148	2.1515	2.15149

We consider again only the symmetric case. For this case $\chi(z)$ and $G_{bb}(z)$ are the odd functions of z. It can be shown that for the symmetric case $\Gamma_{2;\sigma\sigma'}(z,z',z') = \Gamma_{2\,\mathrm{even};\sigma\sigma'}(z,z',z') + \Gamma_{2\,\mathrm{odd};\sigma\sigma'}(z,z',z')$. Here $\Gamma_{2\,\mathrm{odd};\sigma\sigma'}(z,z',z')$ is the odd function of both z and z' and only this part of Γ_2 gives the contribution to δE_{nr} (31). The vertex function $\Gamma_{2\mathrm{odd};\sigma\sigma'}(z,z',z')$ determines also the self-energy $\Delta\Sigma^{(2)}(z)$ and is given by

$$
\sum_{\sigma,\sigma'} G_{ab}^{2}(z)\Gamma_{2\,\mathrm{odd};\sigma\sigma'}(z,z',z')G_{ab}^{2}(z') = -\frac{24x^{2}V^{4}z}{[(z^{2}-d_{-}^{2})(z^{2}-d_{+}^{2})]^{2}}[\Psi(z,\varepsilon)-\Psi(z,-\varepsilon)] \tag{32}
$$

where $\Psi(z,\varepsilon) = R(z,\varepsilon)/[P(z,\varepsilon)(\varepsilon + d_-)^2(\varepsilon + d_+)^2]$ and the functions $R(z,\varepsilon)$ and $P(z,\varepsilon)$ are defined by equations (28-29) of [21].

To check the accuracy of our approximations, we calculate the chemisorption energies E_{r} and $E_{\mathrm{r}} + \delta E_{\mathrm{nr}}$ for the exactly solvable model of a one-level atom being joined to the end of a chain consisting of three metal atoms [23]. In Table 1 we compare our results with the exact ones presented in reference [14] and with the chemisorption energies E_{v} obtained using a variation Ansatz for the ground state of the Anderson Hamiltonian [14]. The energies are given in units of $2T$ where T is the hopping integral between nearest neighbors in the metal chain. From Table 1 it follows that for $V \geq 0.375$ the rather accurate variation method of reference [14] and our diagram method for δE_{nr} yield the chemisorption energies with about the same accuracy.

In Table 2 we also compare our results with the exact ones for the same finite-chain model of adsorption and with the chemisorption energies E_{in} obtained in [31] using the interpolation method of reference [33]. The energies are given in units of T. Table 2 shows that even for $V = 1$

Table 2. The chemisorption energies E_{r}, $E = E_{\mathrm{r}} + \delta E_{\mathrm{nr}}$, the exact chemisorption energies E_{exact} and the energies E_{in} of reference [31] obtained using the interpolation method of reference [33] for the finite chain model of adsorption. $U = 8$, $\varepsilon_a = -U/2$ and $T = 1$.

V	$-E_{\mathrm{r}}$	$-E$	$-E_{\mathrm{exact}}$	$-E_{\mathrm{in}}$
1	0.5662	0.5791	0.5785	0.5770
3	3.7573	3.7583	3.7583	3.7584
5	7.5394	7.5395	7.5395	7.5395

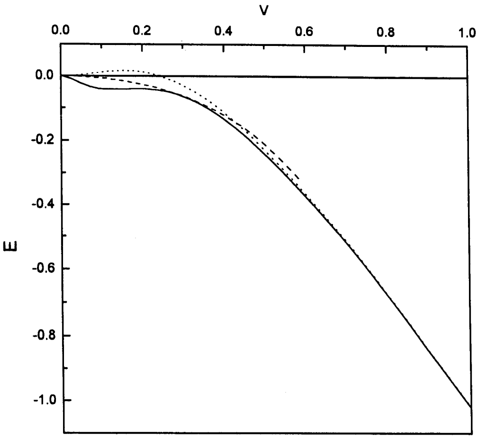

Fig. 2. The chemisorption energies E_{r} in RDA (dotted line), $E = E_{\mathrm{r}} + \delta E_{\mathrm{nr}}$ (solid line) and $E_{\mathrm{wc}} = (\Delta E_{\mathrm{r}})_{\mathrm{wc}} + (\Delta E_{\mathrm{nr}}^{(4)})_{\mathrm{wc}}$ (dashed line) as functions of V. $U = 2.5$, $\varepsilon_a = -U/2$, $B = 2$.

the energy E reproduces the exact results with better accuracy than the method of reference [33].

Figure 2 shows the chemisorption energies E_{r} (dotted line) and $E_{\mathrm{r}} + \delta E_{\mathrm{nr}}$ (solid line) as functions of V for the symmetric case for the hydrogen adsorption on a metal having the semi-elliptic density of states $\Delta(\varepsilon)$ suggested in [13]. The parameter U has been chosen to be 2.5 [14], the bandwidth $B = 2$. The energy E_{r} for the cases $|M_1| = M_2 < 1$ (or $V < 1/3$) has been calculated using the analytical continuation of the function $E_{\mathrm{r}}(V)$ (23). The original equation (17) can also be used. The dashed line presents the chemisorption energy

$$E_{\mathrm{wc}}(V) = (\Delta E_{\mathrm{r}})_{\mathrm{wc}} + (\Delta E_{\mathrm{nr}}^{(4)})_{\mathrm{wc}} \tag{33}$$

in the weak-coupling limit. As has been shown in [21], for the calculations of the energies $(\Delta E_{\mathrm{r}})_{\mathrm{wc}}$ and $(\Delta E_{\mathrm{nr}}^{(4)})_{\mathrm{wc}}$ it is sufficient to substitute in equations (17) and (27) the function $\Gamma(z) = \pi V^2 \Lambda(z)$ instead of $\chi(z)$, the function $G_{aa\sigma}(z)$ for $V = 0$ instead of $G_{bb\sigma}(z)$ and $G_{ba\sigma}(z)$, and the self-energy $\Delta\Sigma_{\mathrm{wc}}^{(2)}(z)$ given by equation (31) of reference [21] instead of $\Delta\Sigma^{(2)}(z)$.

When V decreases and tends to $V_* \approx 0.3$, the curve $E(V)$ is almost tangential to the curve $E_{\mathrm{wc}}(V)$ with the accuracy of 0.001 (or 1.6% of $E(V_*)$) and interpolates approximately between the strong-coupling and weak-coupling limits. For $V < 0.3$ the curve $E(V)$ deviates from $E_{\mathrm{wc}}(V)$, and for small values of V behaves like $V^2 \ln(V)$. For $U = 1$ the curves $E(V)$ and $E_{\mathrm{wc}}(V)$ are approximately tangents at $V_* = 0.2$.

This interpolation property of the function $E(V)$ is connected with the next important feature of the diagram technique based on the perturbation expansion in the rebonding interaction [20]. Since $G_{ab}(z) \sim V G_{aa}(z)$ (see Eq. (9)), the contributions of the diagrams, which contain the vertex function Γ_k with $k > 2$ or more than one vertex functions Γ_2, have additional factors $(G_{ab})^2 \sim V^2$ in comparison with the energy δE_{nr}. Therefore, the total contribution of these diagrams is small under the condition $V > V_*(U)$.

More precisely, for the semi-elliptic density of states $\Delta(\varepsilon)$ the absolute value $|\gamma(\mathrm{i}\omega)||$ of the effective interaction parameter $\gamma(z) = G_{ab}(z)\chi(z)G_{ba}(z)$ on the imaginary axis $\mathrm{Re}\, z = 0$, $\mathrm{Im}\, z = \omega \geq 0$ is given by

$$|\gamma(\mathrm{i}\omega)| = \frac{0.5V^2\left[(\omega^2+1)^{1/2} - \omega\right](\omega^2 + 9V^2)^2}{\left[\omega^4 + 2\omega^2(2x^2 + 5V^2) + 9V^4\right]^2} \tag{34}$$

and is the decreasing function of ω for $\omega \geq 0$. For any U and arbitrary symmetric function $\Delta(\varepsilon)$ from equation (16) we have that

$$|\gamma(0)| = |\chi(0)|/V^2 = 1/\pi\Delta(0)V^2. \tag{35}$$

Therefore, for a given V and the density of states function with a large value of $\Delta(0)$ the metal-adatom system is close to the SM limit and $|\gamma(0)|$ is small. For the semi-elliptic $\Delta(\varepsilon)$ the absolute value $|\gamma(0)| = 1/2V^2$, so that for $V > 2^{-1/2}$ and all values of ω the function $|\gamma(\mathrm{i}\omega)| < 1$. For $V = 0.5$ $|\gamma(0)|$ is equal to 2, but for small values of V the function $|\gamma(\mathrm{i}\omega)| < 1$ decreases abruptly because for $\omega \sim 1$ we already have $|\gamma(\mathrm{i}\omega)| \sim V^2$. Thus, it can be supposed that for $V \sim 0.5$ the small neighborhood of the point $\omega = 0$ does not give yet the appreciable contribution to the integrals entering the expressions for the diagrams which contain the vertex function Γ_k with $k > 2$ or more than one vertex function Γ_2.

The appearance of the function $V_*(U)$ is caused by the presence of the energy d_- in the denominators of $G_{ij}(z)$ and Γ_2. When V decreases, the energy d_- decreases too and for values of V smaller than some $V_*(U)$ begins to play the main role during the integration in equation (31). As a result, the curve $E(V)$ deviates from $E_{\mathrm{wc}}(V)$ for $V < V_*(U)$. For $U < 8$ the energy d_- has the order of V for $V \sim 1$. For small values of V we have $d_- \approx -6V^2/U$ and therefore $V_*(U) \sim U^{1/2}$. In the limit $U \to 0$ both $V_*(U)$ and δE_{nr} tend to zero, and $E(V)$ goes to the exact chemisorption energy for the case of non-interacting electrons.

We present also the set of characteristic energies for $V = 0.5$, $U = 2.5$ and semi-elliptic density of states: $E_{\mathrm{r}} = -0.228$, $E = -0.240$, $\Delta E_{\mathrm{r}}^{(2)} = -0.343$, $\Delta E_{\mathrm{r}}^{(4)} = 0.040$, $\Delta E_{\mathrm{nr}}^{(4)} = -0.018$, $\delta E_{\mathrm{nr}} = -0.012$. Figure 1 and Table 1 show that for $V > 0.5$, RDA works rather well.

5 Hydrogen chemisorption energies on transition metals

As an application of our diagram technique, we calculate hydrogen chemisoprion energies on polycrystalline transition metal surfaces and explain their trends along the transition metal series using the surface molecule point of view. This explanation is rather simple since the energies ΔE_{20}, E_b and ΔE_{r} entering expression (6) for the chemisorption energy are simple functions of the electronic properties of transition metals. The properties under consideration are the width B of the d band, the position of the Fermi level ε_{F} with respect to the d band center and the work function A. The value of the work function enters the problem in the implicit form through the value of ε_a which is given by the expression [1]

$$\varepsilon_a = -13.6 \text{ eV} + W_{\mathrm{im}} + \varepsilon_{\mathrm{F}} + A \tag{36}$$

where W_{im} is the image potential and ε_a is measured from the d band center.

We take into account only d bands of transition metals because recent calculations of adsorption systems have shown that, *e.g.* for Pd covalent bonds result mainly from the hybridization of H $1s$ and Pd $4d$ states [2]. Ni $3d$ states also give a strong admixture to the bonding [35,36]. The metal parameters were taken to be the same as in reference [11].

We calculate the hydrogen chemisorption energies for hydrogen equilibrium positions. Therefore, we do not consider the repulsion energy [10] which is necessary to find an equilibrium position but is omitted in the Anderson-Newns model. From the inhomogeneous electron gas theory [37] it can be concluded that the energies V, U and W_{im} being considered as the ground state properties of the H/Me system are functionals of the electronic density. Further on, using the ideas of the effective medium theory [11], we may also consider V, U and W_{im} as functions of the average electron density $\overline{n}_0$ at the equilibrium position. Since this density is the same for all transition metals [11], we assume below that the energies U and W_{im} are also the same for all transition metals and equal to 4 eV and 5.5 eV, respectively. These values are often used to imitate hydrogen chemisorption on transition metals within the Anderson-Newns model [38,39].

The hopping parameter V is taken to be the same along a transition metal series with a given number. However, it is considered as a function of a number of series and is chosen to reproduce within RDA the experimental hydrogen chemisorption energy E_{exp} for one of the metals from a given series. The semi-elliptic density of states is used in our calculations because it approximates rather well the surface density of states of transition metals having both fcc structure and bcc structure in the case when the latter have the surface states (see *e.g.* the results of calculations of local densities of states for Mo and W presented in Ref. [40]). Using the experimental hydrogen chemisorption energies [41] for H/Ni(111) ($E_{\mathrm{exp}} = -2.7$ eV), H/Mo(110) ($E_{\mathrm{exp}} = -2.97$ eV) and H/W(100) ($E_{\mathrm{exp}} = -2.94$ eV), one finds that $V_{3d} = 2.382$ eV, $V_{4d} = 2.712$ eV and $V_{5d} = 2.846$ eV for $3d$, $4d$ and $5d$ transition metals, respectively. The obtained hierarchy of values of V reflects that of the decay lengths of the corresponding d wave-functions.

Table 3. Hydrogen chemisorption energies E_{r}, $E = E_{\mathrm{r}} + \Delta E^{(4)}_{\mathrm{nr}}$ and E_{exp} for $5d$ transition metals. The experimental chemisorption energies E_{exp} are taken from references [11,41]. The band parameters are the same as in reference [11]. B is the width of the d band, the energies ε_{F} and ε_a are measured from the d band center, the correlation energy $\varepsilon_{\mathrm{c}} = E_{\mathrm{HF}} - E$. The other energies are defined in the paper. All the energies are given in eV. $U = 4$ eV, $V = 2.846$ eV.

Metal	Hf	Ta	W	Re	Os	Ir	Pt
B	10.2	11.6	11.7	11.4	10.7	9.2	7.3
ε_{F}	−2.67	−2.36	−0.42	0.57	1.68	2.72	2.90
ε_a	−6.87	−5.96	−4.02	−2.83	−0.52	0.12	0.44
$-\Delta E_{20}$	6.162	5.708	5.026	4.820	4.912	5.051	5.138
E_b	3.702	4.002	3.734	3.646	3.574	3.457	3.130
$-\Delta E_{\mathrm{r}}$	0.859	1.258	1.648	1.710	1.428	1.173	0.754
$-\Delta E^{(2)}$	0.825	1.260	1.742	1.838	1.518	1.245	0.787
$\Delta E^{(4)}$	−0.027	0.016	0.093	0.165	0.162	0.255	0.140
$-\Delta E^{(4)}_{\mathrm{nr}}$	0.014	0.025	−0.007	0.023	0.063	0.177	0.102
$-E_{\mathrm{r}}$	3.32	2.96	2.94	2.88	2.77	2.77	2.76
$-E$	3.31	2.94	2.95	2.86	2.71	2.6	2.66
$-E_{\mathrm{exp}}$			2.94	2.9		2.52 2.73	2.6
ε_{c}	0.05	0.06	0.1	0.1	0.1	0.04	0.06

In Table 3 we present the results of calculations of hydrogen chemisorption energies for the $5d$ transition metal series. Similar results were also obtained for $3d$ and $4d$ series. The energies ΔE_{20} and E_b are calculated exactly using equation (14) and equation (A.8) of the Appendix. The energy ΔE of the interaction of SM with the remaining metal is calculated in RDA. The hydrogen chemisorption energy E includes also the correction $\Delta E^{(4)}_{\mathrm{nr}}$ to E_{r} where E_{r} is calculated using equation (23). From Table 3 it follows that for constant V, U and W_{im} the absolute values of the chemisorption energies E_{r} and E decrease in the whole with the increase of the serial number of a metal. A local minimum of $|E|$ is obtained for iridium. The same tendency is also observed in experiment. Since $|E^{(4)}| \ll |\Delta E^{(2)}|$, the perturbation expansion in the rebonding interaction yields rather accurate results. The accuracy of calculations may be estimated as $0.1\ |\Delta E^{(4)}| \sim 0.01$ eV. Since $U/4V \approx 0.35$, the correlation energies ε_{c} are small at the equilibrium positions. These energies are the largest at the middle of the series near the symmetric case $\varepsilon_a = -U/2$, as it should be for $U < 6.7V$ [29].

Similar results for the chemisorption energy have been previously obtained in references [7,11] using other methods of calculation. These results are in accordance with the general experimental observation that hydrogen chemisorption energy decreases along the transition metal series [42].

Now we explain the trends in hydrogen chemisorption energy along the transition metal series in terms of the energies ΔE_{20}, E_b and ΔE. The binding energy of the doubly-occupied SM ΔE_{20} is an even function of $t = \varepsilon_a + U/2$ (see Eq. (14)) and takes its smallest absolute value at $t = 0$. The energy ΔE_{20} as a function of t is shown in Figure 3 for three values of V. The general behavior of $\Delta E_{20}(t)$ is the same as for $U = 0$ (in this case

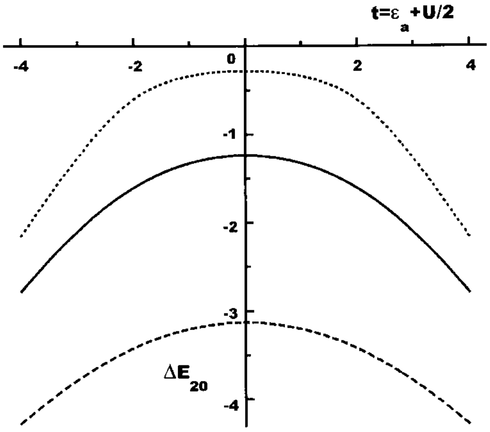

Fig. 3. The binding energy of the doubly occupied surface molecule ΔE_{20} as a function of $t = \varepsilon_a + U/2$ for $U = 4$ and different values of V: $V = 0.4$ (dotted line), $V = 1$ (solid line) and $V = 2$ (dashed line).

$\Delta E_{20}(t) = -(t^2 + 4V^2)^{1/2})$ and has a simple physical meaning. It is energetically favorable for both electrons to occupy the state $|a\rangle$ for $t < 0$ and, on the contrary, it is energetically favorable for both electrons to occupy the state $|b\rangle$ for $t > 0$. The value of ε_a is given by equation (36) where only the Fermi energy ε_F and the work function A depend on the nature of the metal. The Fermi energy increases along the transition metal series due to the d band filling. The work function A also increases with the increase of the serial number of a transition metal in a given series what is connected with the rise of the first ionization energy of a free metal atom due to the increase of its nuclear charge [43]. Thus, the values of A are small and the values of ε_F are negative at the beginning of the series. It results in a large negative ε_a (see Tab. 3) and, therefore, in large absolute values of ΔE_{20}. Just this effect explains the relatively large absolute values of hydrogen chemisorption energies at the beginning of the series.

The dimensionless energy E_b as a function of ε_F is shown in Figure 4 by a solid line for the semi-elliptic density of states (the discussion of Fig. 4 in detail is presented in the Appendix). It is an even function of ε_F and has a minimum at $\varepsilon_F = 0$. The width B of the d band reaches its maximum value near the middle of the series (Mo, W) (see Tab. 3) which is similar to the behavior of a metal binding energy and is connected with the filling of the metal bonding states. As a result, the effect of B on E_b is dominant and the energy E_b given in eV takes the maximum value for Ta.

The energy E_b decreases at the end of the series. On the contrary, the energy $|\Delta E_{20}|$ increases slightly so that the sum $|\Delta E_{20} + E_b|$ increases at the end of the series too. However, this increase is compensated by the decrease of the absolute value of $|\Delta E_r|$ at the end of the series. Since the SM limit takes place for $B = 0$, the absolute value of the interaction energy of SM with the remaining metal $|\Delta E_r|$ reaches its maximum near the center of the series for metals having the large width of the d band (see Tab. 3). As a result, the energy $|E_r|$ decreases in the whole along the transition metal series and is almost constant at the end of the series due to the compensation discussed above. However, the correction $\Delta E_{nr}^{(4)}$ increases at the end of the series due to the d band filling so that the hydrogen chemisorption energy $|E|$ is minimal for the metals of the platinum group. It should be noted that the energies ΔE_{20}, E_b and ΔE_r do not change monotonously with the d band filling. However, the energies $|E_r|$ and $|E|$ decrease in the whole along the transition metal series.

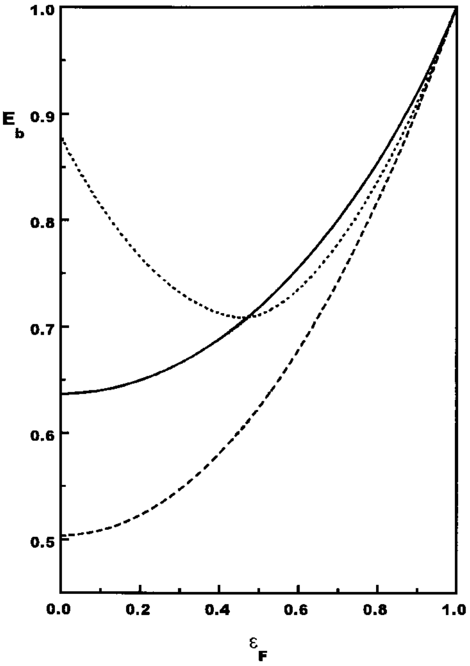

Fig. 4. The energy E_b of the separation of the singly occupied state $|b\rangle$ from a metal as a function of ε_F for three densities of states $\Delta(\varepsilon)$: $\Delta(\varepsilon) = (2/\pi)(1 - \varepsilon^2)^{1/2}$ (the semi-elliptic density of states, solid line), $\Delta(\varepsilon) = (8/3\pi)(1-\varepsilon^2)^{3/2}$ (dashed line) and the double-triangle density of states (Eq. (A.7), dotted line). E_b and ε_F are measured in units of $B/2$.

At the end of this section we compare our explanation of trends in hydrogen chemisorption energy with the others in literature. As is concluded in reference [44], the decrease of the binding energy of a number of species with transition metals is due to the progressive filling of the antibonding levels of SM formed in the strong coupling limit of adsorption. However, our study shows that the SM energy levels are not "frozen" with the d band filling. On the contrary, the energy $|\Delta E_{20}|$ increases at the end of the series, and the overall trends in hydrogen chemisorption energy is a result of the concerted behavior of the energies ΔE_{20}, E_b and ΔE.

In the effective medium theory [11] the starting point is the hydrogen atom in a homogeneous electron gas which includes the metal d electrons. Therefore, the energy ΔE^{hom} [11] which is the same for all transition metals includes also the contribution of d electrons. In the homogeneous electron gas the hydrogen 1s level is always shifted down to just below the bottom of the band and is doubly occupied. In this case the energy ΔE^{hyb} describing additional hybridization of the adatom electrons with the metal d electrons is rather small and accounts for the weak variation of hydrogen chemisorption energy with the band filling.

On the contrary, in our approach: (1) the bare hydrogen $1s$ level is singly occupied; (2) the energies ΔE_{20} and ΔE include hybridization of the adatom electron with the metal d electrons; (3) all the energies ΔE_{20}, E_b and ΔE change with the d band filling. Therefore, our approach takes into account the d band structure effects from the very beginning and can be considered as complementary to the method of reference [11].

6 Conclusion

Using the perturbation expansion in the rebonding interaction near the surface molecule limit, the new diagram technique for the calculation of the chemisorption energy in the Anderson model is proposed. The new expression for the chemisorption energy in RDA is presented. RDA is exact in the limits when $B = 0$ or $U = 0$. It gives also the exact second-order contribution of the rebonding interaction and is exact up to the first order in $|\varepsilon_a|^{-1}$ for $|\varepsilon_a| \to \infty$. It should be noted that for the perturbation expansion in the hybridization the approximation analogous to RDA is of no importance because in this case $|(\Delta E_{\rm r}^{(4)})_{\rm wc}|$ is always smaller than $|(\Delta E_{\rm nr}^{(4)})_{\rm wc}|$. In particular, it can be shown that $(\Delta E_{\rm nr}^{(4)})_{\rm wc} \approx -4V^4/U$ for $V \to 0$ so that the allowable values of V should satisfy the condition $V^4 \ll U$.

The expression for the contribution of the non-ring diagram of the fourth order in the rebonding interaction and the approximate expression for the contribution of the higher-order non-ring diagrams are obtained. It is shown that our diagram method yields rather accurate chemisorption energies at least for such values of V, U which imitate hydrogen chemisorption on transition metals. In particular, RDA is more simple and convenient in the asymmetric case in comparison with other methods (see *e.g.* the method of Ref. [33]).

Finally, the diagram technique suggested in the present paper provides the foundation of the simple and transparent physical picture of hydrogen chemisorption on transition metals. It consists in the formation of SM and its subsequent interaction with the remaining metal. Based on this picture, a simple explanation of observable trends in hydrogen chemisorption energy is given.

Appendix

In this Appendix we study the dependence of the energy $E_b(\varepsilon_{\rm F})$, which has a physical meaning of the energy of the separation of the singly-occupied state $|b\rangle$ from the metal, on the form of the density of states $\Delta(\varepsilon)$. This study is of interest since, in general, various functions $\Delta(\varepsilon)$ correspond to different group orbitals $|b\rangle$ in the case of chemisorption of a one-level atom on different crystal faces of transition metals at different positions [45]. For the sake of simplicity we consider below only even functions $\Delta(\varepsilon)$ *i.e.* the density of states which are symmetric with respect to the d band center. In this case the energy $E_b(\varepsilon_{\rm F})$ is an even function of $\varepsilon_{\rm F}$.

It can be shown from equation (22) that the energy $E_b(\varepsilon_{\rm F})$ obeys the next inequalities:

$$|\varepsilon_{\rm F}| \le E_b(\varepsilon_{\rm F}) \le 2 - |\varepsilon_{\rm F}|. \qquad \text{(A.1)}$$

To study the general properties of $E_b(\varepsilon_{\rm F})$, it is worthwhile considering a family of density of states functions $\Delta_{a,c}(\varepsilon, \eta)$ which tend to the family of functions

$$\Delta_{a,c}(\varepsilon) = (2+c)^{-1}[\delta(\varepsilon - a) + c\delta(\varepsilon) + \delta(\varepsilon + a)] \qquad \text{(A.2)}$$

when the widths of their peaks, which are proportional to η, tend to zero. Here $0 \le a \le 1$, $c \ge 0$. Then from equation (22) we get that the energy $E_b(\varepsilon_{\rm F})$ for $\Delta(\varepsilon) = \Delta_{a,c}(\varepsilon, \eta)$ tends to $E_{b*}(\varepsilon_{\rm F})$ when $\eta \to 0$

$$E_{b*}(\varepsilon_{\rm F}) = \begin{cases} E_{b*}(0) + \varepsilon_{\rm F}, & \varepsilon_{\rm F} \le \beta a \\ 2a - \varepsilon_{\rm F} & \beta a \le \varepsilon_{\rm F} \le a \\ \varepsilon_{\rm F}, & \varepsilon_{\rm F} \ge a \end{cases} \qquad \text{(A.3)}$$

where $E_{b*}(0) = 2(1-\beta)a$, $\beta = c^{1/2}(2+c)^{-1/2}$ and $\varepsilon_{\rm F} \ge 0$.

When $a = 0$, we have $\Delta_{0,c}(\varepsilon) = \delta(\varepsilon)$ and the energy $E_{b*}(\varepsilon_{\rm F})$ is equal to the lower boundary $|\varepsilon_{\rm F}|$ of energies $E_b(\varepsilon_{\rm F})$ (see Eq (A.1)). On the contrary, $\Delta_{a,c}(\varepsilon) = [\delta(\varepsilon - 1) + \delta(\varepsilon + 1)]/2$ for $a = 1$, $c = 0$ and the energy $E_{b*}(\varepsilon_{\rm F})$ is equal to the upper boundary $2 - |\varepsilon_{\rm F}|$ of energies $E_b(\varepsilon_{\rm F})$.

A family of functions (A.2) can be considered as a limiting case of a number of density of states functions which are often used to imitate hydrogen chemisorption on transition metals. Therefore, one can approximately obtain from equation (A.3) a form of corresponding curves $E_b(\varepsilon_{\rm F})$. To illustrate the dependence of $E_b(\varepsilon_{\rm F})$ on the form of $\Delta(\varepsilon)$, we use below the semi-elliptic density of states [13]

$$\Delta(\varepsilon) = \frac{2}{\pi}(1 - \varepsilon^2)^{1/2}\theta(1 - |\varepsilon|) \qquad \text{(A.4)}$$

where $\theta(x)$ is a step function, the density of states of reference [7]

$$\Delta(\varepsilon) = \frac{8}{3\pi}(1 - \varepsilon^2)^{3/2}\theta(1 - |\varepsilon|), \qquad \Lambda(\varepsilon) = \frac{8}{3\pi}\rho(\varepsilon), \qquad \text{(A.5)}$$

where

$$\rho(\varepsilon) = \begin{cases} \frac{3}{2}\varepsilon - \varepsilon^3, & |\varepsilon| \le 1 \\ \frac{3}{2}\varepsilon - \varepsilon^3 - (\varepsilon^2 - 1)^{3/2}, & \varepsilon \le 1 \\ \frac{3}{2}\varepsilon - \varepsilon^3 + (\varepsilon^2 - 1)^{3/2}, & \varepsilon \ge 1 \end{cases} \qquad \text{(A.6)}$$

and the density of states which has a form of two isosceles triangles and is a symmetric variant of that used in reference [38]:

$$\Delta(\varepsilon) = \theta(1 - |\varepsilon|)\begin{cases} 1 - |2\varepsilon - 1|, & 0 \le \varepsilon \le 1 \\ 1 + |2\varepsilon + 1|, & -1 \le \varepsilon \le 0. \end{cases} \qquad \text{(A.7)}$$

From equation (22) one gets that for the semi-elliptic density of states

$$E_b(\varepsilon_{\mathrm{F}}) = \varepsilon_{\mathrm{F}}[1-(2/\pi)\arccos(\varepsilon_{\mathrm{F}})] + (2/\pi)(1-\varepsilon_{\mathrm{F}}^2)^{1/2} \tag{A.8}$$

where arccos is taken from 0 to π and $E_b(0) = 2/\pi$ and

$$E_b(\varepsilon_{\mathrm{F}}) = -\varepsilon_{\mathrm{F}}\left\{1+\frac{2}{\pi}\mathrm{arctg}\left[\frac{\Delta(\varepsilon_{\mathrm{F}})}{\Lambda(\varepsilon_{\mathrm{F}})}\right]\right\} + \frac{4}{\pi}(1-\varepsilon_{\mathrm{F}}^2)^{1/2} - \frac{4}{\pi 3^{1/2}}\mathrm{arctg}[3^{1/2}(1-\varepsilon_{\mathrm{F}}^2)^{1/2}] \tag{A.9}$$

for the density of states (A.5) where the first arctg in the right-hand side is taken from $-\pi$ to 0, the second one from $-\pi/2$ to $\pi/2$ and $E_b(0) = 4(\pi^{-1} - 3^{-3/2})$.

In Figure 4 presented in Section 5, we showed the energy E_b as a function of ε_{F} for the densities of states given by equations (A.4-A.5) and (A.7). The density of states (A.4-A.5) tend to $\delta(\varepsilon)$ when the bandwidth $B \to 0$. Since the function $\Delta(\varepsilon)$ (A.5) has a more pronounced maximum at the point $\varepsilon = 0$ as compared to the semi-elliptic density of sates, the separation of the singly-occupied state $|b\rangle$ requires more energy for the semi-elliptic $\Delta(\varepsilon)$. The density of states (A.7) tends to the function $\Delta_{1/2,0}(\varepsilon)$ given by equation (A.2) when the basis of the triangles tend to zero. The separation of two localized levels with $\varepsilon_b = \pm 1/2$ is more energetically favorable in this case. The same also takes place for the double-triangle function (A.7). Therefore, the energy $E_b(0)$ for this case is substantially larger than for the densities of states (A.4-A.5) as shown in Figure 4.

It can be also shown that for arbitrary density of states

$$(\mathrm{d}E_b(\varepsilon_{\mathrm{F}})/\mathrm{d}\varepsilon_{\mathrm{F}})_{\varepsilon_{\mathrm{F}}=\pm 1} = \pm 1. \tag{A.10}$$

However, the behavior of the energy $E_b(\varepsilon_{\mathrm{F}})$ for $|\varepsilon_{\mathrm{F}}| > 0.5$ depends on the rate of the tendency of the corresponding density of states function to zero at the top of the d band, so that the larger rate causes the smaller values of $E_b(\varepsilon_{\mathrm{F}})$. Therefore, the curve $E_b(\varepsilon_{\mathrm{F}})$ for the double-triangle density of states occupies the intermediate position between the other curves in the domain $|\varepsilon_{\mathrm{F}}| > 0.5$.

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