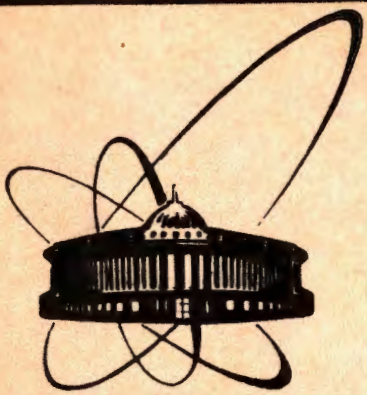

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E17-92-266

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CORRELATION EFFECTS IN CHEMISORPTION THEORY: INFLUENCE OF THE ADATOM ORBITAL OCCUPANCY AND SUBSTRATE ELECTRONS ON THE BINDING ENERGY

Submitted to "Surface Science"

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1992

In the last years a large amount of works devoted to the chemisorption theory has been published [1-5]. Despite many particular results some aspects of the theory are still waiting for a definitive answer, specially those related to the many adatoms case, mainly due to the strong correlation effects present in both the electronic and the ionic components of the system [2-5]. The recently suggested composite Hamiltonian method [6] seems to be a very useful tool in carrying out such tasks as it gives a relatively simple microscopic picture specially suitable not only for describing the experimentally observed features but for understanding the physics of the chemisorption phenomenon. In the framework of this approach the coverage dependence of the single-electron characteristics has been investigated within Hartree-Fock (HF) approximation [2-3] and including electron correlation effects by using the second order self-matrix method of Brenig and Schonhammer [5,7,8].

In this paper we present a formalism for the calculation of the chemisorption energy beyond the HF approximation which in some manner complement the results of the ref. [7]. Our method is based on the statistical perturbation theory and the two-times Green functions formalism [9]. Following [6] we write the Hamiltonian of the system as follows

$$H= \Sigma\varepsilon_k n_{k\sigma}+ \Sigma N_\alpha [\Sigma E_\alpha n_{\alpha\sigma}+Un_{\alpha\sigma}n_{\alpha-\sigma}+ \Sigma(V_{\alpha k}b^+_{\alpha k}a_{k\sigma}+h.c.)] \quad (1)$$

which generalizes the well-known Anderson-Newns Hamiltonian [10] to the case of stochastical submonolayer coverage, the operator N_α takes the values 0 or 1 if the adsorption centre with coordinates r_α is empty (occupied by an impurity ion). The others parametrs are usual parameters of the Anderson model.

Let rewrite (1) as

$$H = H_o + H_{int} , \quad (2)$$

where

$$H = \Sigma \varepsilon_k n_{k\sigma}+ \Sigma N_\alpha E_\alpha n_{\alpha\sigma}+ \Sigma UN_\alpha n_{\alpha\sigma}n_{\alpha-\sigma} ;$$

$$\mathcal{H}_{int} = \sum V_{AK} N_{\alpha k} b^{+}_{\alpha} a_{\alpha\sigma} + b_{k\sigma} c .$$

and consider $\mathcal{H}_{int}$ as a small perturbation with respect to $\mathcal{H}_o$. The change in the binding energy ΔE, induced by $\mathcal{H}_{int}$ can be calculated using the statistical perturbation theory as

$$\Delta E = \langle E(t) \rangle - \langle E(0) \rangle = \delta \langle E(t) \rangle , \qquad (3)$$

where the angle brackets $\langle ... \rangle$, as usual, mean statistical averaging with the grand canonical ensemble with $\mathcal{H}_o = \mathcal{H}_o - \mu N$, and μ, N are the chemical potential and the total number of electrons respectively.

Further we use the two-times retarded Green functions machinery [9] and restrict ourselves to linear in $\mathcal{H}_{int}$ approximation. Suppose that perturbation is turned on adiabatically at moment $t_o = -\infty$, in this case for ΔE we have

$$\delta \langle E(t) \rangle = -2\pi \sum_{\Omega} e^{\zeta t - i\Omega t} \langle\langle \mathcal{H}; \mathcal{H}_{int} \rangle\rangle_{\Omega} , \qquad (4)$$

with $\zeta \to 0$, $\Omega \to 0$ that gives

$$\Delta E = \delta \langle E \rangle = -2\pi \langle\langle \mathcal{H}; \mathcal{H}_{int} \rangle\rangle_{\Omega=0} , \qquad (5)$$

and in the final form

$$\Delta E = -2\pi \sum \{ \langle\langle N_\alpha b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}} \rangle\rangle + \langle\langle N_\alpha a^{+}_{k\sigma} b_{\alpha\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}} \rangle\rangle \} . \qquad (6)$$

The Green functions in (6) can be obtained solving the system

$$(\omega + E_\alpha - \varepsilon_k) \langle\langle N_\alpha b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}} \rangle\rangle = \frac{1}{\pi} \langle [N_\alpha b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}}] \rangle - U \langle\langle N_\alpha n_{\alpha\bar{\sigma}} b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}} \rangle\rangle ;$$

$$(\omega - E_\alpha + \varepsilon_k) \langle\langle N_\alpha a^{+}_{k\sigma} b_{\alpha\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}} \rangle\rangle = \frac{1}{\pi} \langle [N_\alpha a^{+}_{k\sigma} b_{\alpha\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}}] \rangle - U \langle\langle N_\alpha n_{\alpha\bar{\sigma}} a^{+}_{k\sigma} b_{\alpha\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}} \rangle\rangle ;$$

$$(\omega + E_\alpha + U - \varepsilon_k) \langle\langle N_\alpha n_{\alpha\bar{\sigma}} b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}} \rangle\rangle = \frac{1}{\pi} \langle [N_\alpha n_{\alpha\bar{\sigma}} b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}}] \rangle ;$$

$$(\omega - E_\alpha - U + \varepsilon_k) \langle\langle N_\alpha n_{\alpha\bar{\sigma}} a^{+}_{k\sigma} b_{\alpha\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}} \rangle\rangle = \frac{1}{\pi} \langle [N_\alpha n_{\alpha\bar{\sigma}} a^{+}_{k\sigma} b_{k\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}}] \rangle ; \qquad (7)$$

after some straightforward but tedious algebra we obtain the following expression for the Green functions

$$\langle\langle N_\alpha b^{+}_{\alpha\sigma} a_{k\sigma}; N_\beta a^{+}_{k\bar{\sigma}} b_{\beta\bar{\sigma}} \rangle\rangle = -\frac{1}{2\pi} \delta_{\alpha\beta} \delta_{kk} \delta_{\sigma\bar{\sigma}} \{ (\omega - E_\alpha + \varepsilon_k)^{-1} \times$$

$$\times [\langle N_\alpha n_{\alpha\sigma} \rangle - 2\langle N_\alpha n_{\alpha\sigma} n_{k\bar{\sigma}} \rangle + \langle N_\alpha n_{k\bar{\sigma}} \rangle - \langle N_\alpha n_{\alpha\bar{\sigma}} n_{\alpha\sigma} \rangle + 2\langle N_\alpha n_{\alpha\sigma} n_{\alpha\bar{\sigma}} n_{k\bar{\sigma}} \rangle -$$

$$- \langle N_\alpha n_{k\bar{\sigma}} n_{\alpha\bar{\sigma}} \rangle] + (\omega - E_\alpha - U + \varepsilon_k)^{-1} [\langle N_\alpha n_{\alpha\bar{\sigma}} n_{\alpha\sigma} \rangle - 2\langle N_\alpha n_{\alpha\bar{\sigma}} n_{\alpha\sigma} n_{k\bar{\sigma}} \rangle +$$

$$+ \langle N_\alpha n_{\alpha\bar{\sigma}} n_{k\bar{\sigma}} \rangle] \} ;$$

$$\langle\langle N_\alpha a^{+}_{k\sigma} b_{\alpha\sigma}; N_\beta b^{+}_{\beta\bar{\sigma}} a_{k\bar{\sigma}} \rangle\rangle = \frac{1}{2\pi} \delta_{\alpha\beta} \delta_{kk} \delta_{\sigma\bar{\sigma}} \{ (\omega + E_\alpha - \varepsilon_k)^{-1} \times$$

$$\times [\langle N_\alpha n_{\alpha\sigma} \rangle - 2\langle N_\alpha n_{\alpha\sigma} n_{k\bar{\sigma}} \rangle + \langle N_\alpha n_{k\bar{\sigma}} \rangle - \langle N_\alpha n_{\alpha\bar{\sigma}} n_{\alpha\sigma} \rangle + 2\langle N_\alpha n_{\alpha\sigma} n_{\alpha\bar{\sigma}} n_{k\bar{\sigma}} \rangle -$$

$$- \langle N_\alpha n_{k\bar{\sigma}} n_{\alpha\bar{\sigma}} \rangle] + (\omega + E_\alpha + U - \varepsilon_k)^{-1} [\langle N_\alpha n_{\alpha\bar{\sigma}} n_{\alpha\sigma} \rangle - 2\langle N_\alpha n_{\alpha\bar{\sigma}} n_{\alpha\sigma} n_{k\bar{\sigma}} \rangle +$$

$$+ \langle N_\alpha n_{\alpha\bar{\sigma}} n_{k\bar{\sigma}} \rangle] \} , \qquad (8)$$

where the correlation functions $\langle N_\alpha n_{\alpha\sigma} \rangle$, $\langle N_\alpha n_{k\sigma} \rangle$, $\langle N_\alpha n_{\alpha\sigma} n_{k\sigma} \rangle$ appearing in (8) describe the electronic properties of the system and they are defined by the following set of Green function equations

$$(\omega - \varepsilon_k + \mu) \langle\langle N_\alpha a_{k\sigma}; a^{+}_{k\sigma} \rangle\rangle = \frac{\langle N_\alpha \rangle}{2\pi} ;$$

$$(\omega - E_\alpha + \mu) \langle\langle N_\alpha b_{\alpha\bar{\sigma}}; b^{+}_{\alpha\bar{\sigma}} \rangle\rangle = \frac{\langle N_\alpha \rangle}{2\pi} + U \langle\langle N_\alpha n_{\alpha\sigma} b_{\alpha\bar{\sigma}}; b^{+}_{\alpha\bar{\sigma}} \rangle\rangle ;$$

$$(\omega - E_\alpha - U + \mu) \langle\langle N_\alpha n_{\alpha\sigma} b_{\alpha\bar{\sigma}}; b^{+}_{\alpha\bar{\sigma}} \rangle\rangle = \frac{\langle N_\alpha n_{\alpha\sigma} \rangle}{2\pi} ;$$

$$(\omega - E_\alpha + \mu) \langle\langle N_\alpha b_{\alpha\sigma}; b^{+}_{\alpha\sigma} \rangle\rangle = \frac{\langle N_\alpha \rangle}{2\pi} - U \langle\langle N_\alpha n_{\alpha\bar{\sigma}} b_{\alpha\sigma}; b^{+}_{\alpha\sigma} \rangle\rangle ;$$

$$(\omega - E_\alpha - U + \mu) \langle\langle N_\alpha n_{\alpha\bar{\sigma}} b_{\alpha\sigma}; b^{+}_{\alpha\sigma} \rangle\rangle = \frac{\langle N_\alpha n_{\alpha\bar{\sigma}} \rangle}{2\pi} ;$$

$$(\omega - \varepsilon_k + \mu) \langle\langle N_\alpha n_{\alpha\bar{\sigma}} a_{k\sigma}; a^{+}_{k\sigma} \rangle\rangle = \frac{\langle N_\alpha n_{\alpha\bar{\sigma}} \rangle}{2\pi} ;$$

$$(\omega - \varepsilon_k + \mu) \langle\langle N_\alpha n_{\alpha\sigma} a_{k\sigma}; a^{+}_{k\sigma} \rangle\rangle = \frac{\langle N_\alpha n_{\alpha\sigma} \rangle}{2\pi} ; \qquad (9)$$

which finally gives

$$\langle N_\alpha n_{\alpha\sigma}\rangle = \langle N_\alpha n_{\alpha-\sigma}\rangle = \frac{f_1}{1+f_1-f_2}\langle N_\alpha\rangle ;$$

$$\langle N_\alpha n_{\alpha\sigma} n_{\alpha-\sigma}\rangle = \langle N_\alpha n_{\alpha-\sigma} n_{\alpha\sigma}\rangle = \frac{f_1 f_2}{1+f_1-f_2}\langle N_\alpha\rangle ; \qquad (10)$$

$$\langle N_\alpha n_{\alpha\sigma} n_{\alpha-\sigma} n_{k\sigma}\rangle = \langle N_\alpha n_{\alpha-\sigma} n_{\alpha\sigma} n_{k\sigma}\rangle = \frac{f_1 f_2 f_3}{1+f_1-f_2}\langle N_\alpha\rangle ;$$

$$\langle N_\alpha n_{\alpha\sigma} n_{k\sigma}\rangle = \langle N_\alpha n_{\alpha-\sigma} n_{k\sigma}\rangle = \frac{f_1 f_3}{1+f_1-f_2}\langle N_\alpha\rangle ;$$

$$\langle N_\alpha n_{k\sigma}\rangle = \langle N_\alpha\rangle f_3 ,$$

where $f_1=\{\exp[\beta(E_\alpha-\mu)]+1\}^{-1}$; $f_2=\{\exp[\beta(E_\alpha+U-\mu)]+1\}^{-1}$;

$$f_3=\{\exp[\beta(\varepsilon_k-\mu)]+1\}^{-1}. \qquad (11)$$

As can be seen from (10) the adatom electron states with spins ``up`` and ``down`` are equivalent. Finally we obtain for Green functions in (8)

$$\langle\langle N_\alpha a^+_{k\sigma} b_{\alpha\sigma}; N_\beta b^+_{\beta\sigma} a_{k-\sigma}\rangle\rangle = \frac{\langle N_\alpha\rangle}{2\pi}\delta_{\alpha\beta}\delta_{kk}\delta_{-\sigma\sigma}\{(\omega-E_\alpha+\varepsilon_k)^{-1}\times$$

$$\times\frac{(1-f_2)(f_1+f_3-2f_1f_3)}{1+f_1-f_2} + (\omega-E_\alpha-U+\varepsilon_k)^{-1}\frac{f_1(f_2+f_3-2f_2f_3)}{1+f_1-f_2}\} ;$$

$$\langle\langle N_\alpha b^+_{\alpha\sigma} a_{k\sigma}; N_\beta a^+_{k-\sigma} b_{\beta\sigma}\rangle\rangle = \frac{\langle N_\alpha\rangle}{2\pi}\delta_{\alpha\beta}\delta_{kk}\delta_{-\sigma\sigma}\{(\omega+E_\alpha-\varepsilon_k)^{-1}\times$$

$$\times\frac{(1-f_2)(f_1+f_3-2f_1f_3)}{1+f_1-f_2} + (\omega+E_\alpha+U-\varepsilon_k)^{-1}\frac{f_1(f_2+f_3-2f_2f_3)}{1+f_1-f_2}\}; \qquad (12)$$

that gives for the binding energy per impurity atom the following expression

$$\Delta E = -2\sum_k |V_{\alpha k}|^2\left\{\frac{F_1}{(\varepsilon_k-E_\alpha)} + \frac{F_2}{(\varepsilon_k-E_\alpha-U)}\right\}, \qquad (13)$$

where

$$F_1 = \frac{(1-f_2)(f_1+f_3-f_1f_3)}{1+f_1-f_2} ; \qquad (14)$$

$$F_2 = \frac{f_1(f_2+f_3-2f_2f_3)}{1+f_1-f_2} ;$$

and f_1, f_2, f_3 are the functions defined in (11).

Finally we make a brief analysis of the obtained expression:

1) Suppose that $f_1 = f_2 = f_3 = f$, then

$$\Delta E = -4\sum |V_{\alpha k}|^2 (1-f) f \left\{\frac{1-f}{\varepsilon_k-E} + \frac{f}{\varepsilon_k-E_\alpha-U}\right\} \qquad (15)$$

for this special case we see that $\Delta E = 0$ for $f = 0$, or 1.

2) If the adatom ionization level lies above the Fermi level ε_F, we obtain $f_1=0$ and

$$\Delta E = -2\sum\frac{|V_{\alpha k}|^2}{\varepsilon_k-E_\alpha} f . \qquad (16)$$

From (16) we see that if $f_3=0$, then $\Delta E=0$ and chemisorption is impossible.

3) Suppose that $f_1=f_2=1$. In this case one has

$$\Delta E = -2\sum |V_{\alpha k}|^2\frac{1-f_3}{\varepsilon_k-E_\alpha-U} \qquad (17)$$

and the energy is fully determined by the substrate electron occupation number. If the substrate band is fully occupied ($f_3=1$). then $\Delta E = 0$ and chemisorption is impossible.

4) If the electron affinity level lies above ε_F, we have $f = 0$ and

$$\Delta E = -2\sum\frac{|V_{\alpha k}|^2}{1+f_1}\left\{\frac{f_1+f_3-2f_1f_3}{\varepsilon_k-E_\alpha} + \frac{f_1f_3}{\varepsilon_k-E_\alpha-U}\right\}. \qquad (18)$$

α) If only the substrate band is fully occupied, then $f_3=1$ and

$$\Delta E = -2\sum\frac{|V_{\alpha k}|^2}{1+f_1}\left\{\frac{1-f_1}{\varepsilon_k-E_\alpha} + \frac{f_1}{\varepsilon_k-E_\alpha-U}\right\}; \qquad (19)$$

β) If $f_1=f_3=1$, then

$$\Delta E = -\sum\frac{|V_{\alpha k}|^2}{\varepsilon_k-E_\alpha-U} ; \qquad (20)$$

5) When the ionization and affinity levels are different sides of the Fermi level ε_f ($E_\alpha<\varepsilon_f$. and $E_\alpha+U^2$. then $f_1= 1$ and $f_2=0$), we obtain

$$\Delta E = -\sum |V_{\alpha k}|^2\left\{\frac{1-f_3}{\varepsilon_k-E_\alpha} + \frac{f_3}{\varepsilon_k-E_\alpha-U}\right\}. \qquad (21)$$

The comparison of (20) and (21) shows that a symmetrical contribution to the chemisorption energy of adatom and substrate electrons depends on the occupancy of the respective levels.

In conclusion we have obtained a very simple expression for the chemisorptin energy in the presence of electron correlation effects, treated within ferst order statistical perturbation theory. It is of great interest to apply the suggested formalism to concrete model systems. Such investigations are being carried out at present.

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Received by Publishing Department
on October 10, 1992.