Revista Mexicana de Física 32 No. 2 (1986) 311-327

SUM RULE FOR THE BINDING ENERGY OF CHEMISORPTION

P. Villaseñor-González
Jesús Urías
and
F. Mejía-Lira

Instituto de Física
Universidad Autónoma de San Luis Potosí
78000 San Luis Potosí, S.L.P. México

(recibido septiembre 26, 1984; aceptado diciembre 4; 1985)

ABSTRACT

A sum rule for the energy of chemisorption, ΔW, of atoms on solid surfaces is derived in a tight-binding scheme. The sum rule involves some *free* local Green functions of the atomic array on the surface responsible for chemisorption and that of the adatom, *i.e.* ΔW can be exactly computed without working out the electronic structure of the chemisorbed system. The sum rule, as applied to chemisorption at a single site in a Bethe lattice, shows that ΔW is controlled by the Fermi energy, the ionization energy of the adatom as measured from the center of the energy band and by the amount of coupling between the adatom and the surface. Contributions to the sum rule from the discrete and continuum parts of the energy spectrum are analized in detail.

Our results are compared with experimental data for hydrogen chemisorption on surfaces of 3d and 4d transition metals. At this point it is argued that mixing of sp and d-states is essential for an appropiate description of chemisorption on transition metals.

RESUMEN

En el esquema de amarre fuerte se deriva una regla de suma para la energía ΔW de adsorción química de átomos sobre la superficie de un sólido. La regla de suma sólo contiene funciones de Green libres: las funciones de Green locales del arreglo atómico superficial que interviene en la adsorción química y la del átomo que se adsorbe. O sea, ΔW puede calcularse exactamente sin tener que resolver la estructura electrónica del sistema compuesto. Al ser aplicada la regla de suma a la adsorción química en un sitio de una red de Bethe, muestra que ΔW es controlada por la energía de Fermi, la energía de ionización del átomo adsorbido medida a partir del centro de la banda y por la intensidad del acoplamiento entre átomo adsorbido y superficie. Se analizan en detalle las contribuciones a la regla de suma provenientes de las partes discreta y continua del espectro de energía.

Los resultados se comparan con datos experimentales para adsorción química de hidrógeno sobre superficies de metales de transición 3d y 4d. En este punto se argumenta que la mezcla de estados sp y d es esencial para una descripción apropiada de la adsorción química en los metales de transición.

1. INTRODUCTION

Some of the most important parameters characterizing atomic chemisorption on metallic surfaces are the number of chemisorption states and their binding energies. These parameters are all measurable by several alternative experimental methods and in a great variety of different situations(1). These measurements have shown that the chemisorption energies of simple gases (H_2, N_2, O_2, CO, NO, etc) follow systematic trends. These trends cry for an explanation but a general theory of chemisorption is still lacking(2). Comparison of simple model predictions with experimental data will certainly help in identifying the main physical mechanisms behind chemisorption.

The purpose of this paper is to discuss in some detail the use and derivation of a sum rule(3,4) for the binding energy of chemisorption ΔW. This sort of sum rules has been extensively studied(5) and when applied to chemisorption(4), the sum rule provides an economic way of relating the binding energy of chemisorption to the electronic properties of the clean solid surface, to the geometry of the chemisorption site and to the adatom parameters (*e.g.* ionization energy), *i.e.*, in order to use the sum rule one only needs some local Green's functions of the *clean* surface and that of the adatom *before* chemisorption. A bridge is provided between a model Hamiltonian for chemisorption and ΔW.

We have used a very simple one band model for chemisorption (adsorption at a single site in a Bethe lattice$^{(6)}$) to test the sum rule and found that ΔW is controlled by the strength of coupling t_a between adatom and solid surface, the ionization energy ε_a of the free atom as measured from the center of the band and the Fermi energy. We belive the sum rule might provide a very simple and clean way (physics stays clear at any step and no alien parameters are invoked) to compute ΔW from more realistic models (*e.g.* as to include self consistency-effects$^{(2)}$ and/or s-d mixing in transition metals). When compared to some other calculations$^{(7)}$, the savings provided by the sum rule are: (i) ΔW is not computed directly as the difference in energy of the chemisorbed system (an infinity number) and that of the uncoupled system (another infinite number). This difference is usually handled through considerations on the modification of the Fermi energy introduced by chemisorption (sic). And, (ii) the detailed electronic structure (*e.g.* local Green's functions, density of states) of the chemisorbed systems needs not to be known to calculate ΔW. However, the energy spectrum (not the density of states) of the chemisorbed system is very important indeed.

The rest of the paper is organized as follows: Section 2 details the procedure to derive the sum rule. Its use is illustrated for the case of chemisorption on a Bethe lattice.

This is the simplest system in which all the interesting features of the sum rule appear and the connection between the model Hamiltonian and the resulting trends in chemisorption are transparent. Results are discussed in Section 3 and, although we know that the model we choose to illustrate the use of the sum rule is very unrealistic, we compare our results to experimental data for hydrogen chemisorption on transition metals$^{(1)}$. This comparison suggests that mixing of sp and d-states might be essential for an appropiate description of chemisorption on transition metals.

in terms of Green's functions is

$$\Delta W \equiv W(t_a) - W(t_a = 0)$$

$$\doteq -\frac{1}{\pi} \sum_{i} \int_{-\infty}^{\varepsilon_F} \omega \,\mathrm{Im}\,[\,G_{ii}(\omega) - G^{o}_{ii}(\omega)]\,d\omega \quad , \qquad (4)$$

where $G_{ii}(\omega)$ and $G^{o}_{ii}(\omega)$ are the local Green's functions at site i after [see Eqs. (2) and (3)] and before [see Eqs. (1)] chemisorption, respectively. The site i=a, *i.e.*, where the adatom is located, must be included in Eq. (4).

At this point it is worth to say that to calculate binding energies by direct use of Eq. (4) is rather impractical. To achieve that, (i) one must know the local Green's functions at adatom and at every site in the solid before and after adsorption, (ii) the series must be truncated at some point far enough from the chemisorption site, (iii) care must be taken when computing a small number from the difference of two very big (infinite in principle) numbers. Here we bypass all these problems by finding a rule to sum up Eq. (4). Before going into the derivation of the sum rule we find useful first to prove the following theorem.

Theorem: Let

$$H = H^{o} + \lambda H^{I} \qquad (5)$$

and

$$H|\kappa) = E_{\kappa}|\kappa) \quad , \qquad (\kappa|\kappa') = \delta_{\kappa\kappa'}$$

where

$$H^{I} = \sum_{\{i,j\}} |i\rangle\langle j| + \text{h.c.} \quad , \qquad (7)$$

the summation over i and j being restricted to some finite set {i,j} and

$|i>$ and $<j|$ may be wave functions of the Wannier type. If conditions is Eqs. (5)-(7) are fulfilled then

$$\frac{\partial E_\kappa}{\partial\lambda} \text{ Im TrG} = \sum_{\{i,j\}} \text{Im}\{G_{ij}(E_\kappa) + G_{ji}(E_\kappa)\} \quad , \tag{8}$$

where Green's functions are defined by $(z\text{-}H)G(z)=1$ and $G_{ij} = <i|G|j>$.

The finite set $\{i,j\}$ in Eq. (8) is the same one than that in Eq. (7). Actually, Eq. (8) is a Green's function disguised version of the Hellmann-Feynman identity$^{(8)}$

$$\frac{\partial E_\kappa}{\partial\lambda} = (\kappa \mid H^I \mid\kappa)$$

$$= \sum_{\{i,j\}} (\kappa|i><j|\kappa) + \text{c.c.} \tag{9}$$

that follows almost immediately from Eqs. (5)-(7). The proof of Eq. (8) follows.

Using the definition of G we can write

$$G_{ij}(z) = \sum_\kappa \frac{A_{ij}\ (\kappa)}{z-E_\kappa+i\sigma} \quad , \tag{10}$$

where

$$A_{ij}\ (\kappa) \equiv <i|\kappa)(\kappa|j> \quad ,$$

with the properties $A_{ij} = A^*_{ji}$ and Tr A=1 . Replacing

$$\sum_\kappa \to \int \rho(E)dE \tag{11}$$

in Eq. (10), and using the formal identity

$$\frac{1}{x+i\sigma} = P\,\frac{1}{x} - i\pi\delta(x) \quad ,$$

we get

$$G_{ij}\ (z) = -i\pi A_{ij}\ (z)\rho(z) + P\int \frac{\rho(E)\ A_{ij}\ (E)}{z - E}\, dE \quad . \qquad (12)$$

From this last equation is easy to see that the density of states $\rho(E)$ introduced in Eq. (11) is $\rho(z) = -\mathrm{Im}\ \mathrm{Tr}\ G(z)/\pi$.

Finally, one gets Eq. (8) from Eq. (9) by using the imaginary part of the symmetric part of Eq. (12), *i.e.*,

$$\mathrm{Im}\ (G_{ij} + G_{ji}) = -\pi\rho(z)\ [A_{ij} + A_{ji}] \quad .$$

Once Eq. (8) has been proven we can go back to our main problem, namely, to find out a rule to sum Eq. (4).

We use Eq. (8) for chemisorption identifying Eq. (3) as λH^I and t_a as λ, and integrating over E from minus infinity up to the Fermi energy E_F:

$$\frac{\partial W}{\partial t_a} = -\,\frac{2}{\pi}\int_{-\infty}^{E_F} dE\ \mathrm{Im}\ \{G_{sa}\ (E) + G_{as}\ (E)\} \quad , \qquad (13)$$

where

$$W = 2\int_{-\infty}^{E_F} \rho(E)\ E\ dE \quad ,$$

and, since the electronic spin is not being considered explicitly in

2. THE SUM RULE AND HOW TO USE IT

2.1. *The sum rule*

Green's functions are a convenient bridge between a Hamiltonian and the electronic properties of a system, the chemisorption binding energy of an atom to a solid surface, in our case. In this section we derive the sum rule that expresses the chemisorption energy in terms of the local Green's functions of the clean surface and that of the free atom.

We define the chemisorption binding energy as the difference of the electronic energy of the chemisorbed system minus the energy of the system where the atom is infinitely far away from the surface. In the last situation, the Hamiltonian can be written as

$$H^{o} = H_{s} + H_{a} \quad , \tag{1}$$

where H_s and H_a are the Hamiltonians for the clean solid surface and for the free atom, respectively. Any matrix element of H^o between solid-surface and atomic wave functions is identically zero. The Hamiltonian for the chemisorbed system is

$$H = H^{o} + H_{ad} \quad . \tag{2}$$

H_{ad} represents the coupling between atom and solid surface and is the part of H responsible for chemisorption. In can be represented in a tight binding scheme as

$$H_{ad} = t_{a} \left(|s\rangle\langle a| + |a\rangle\langle s| \right) \quad , \tag{3}$$

where $|s\rangle$ is any normalized linear combination of Wannier functions associated with the atomic sites on the solid surface responsible for chemisorption, $|a\rangle$ is the adatom state (assumed a single state) and t_a is the strength of coupling between $|s\rangle$ and $|a\rangle$ states.

The chemisorption binding energy, as defined above, expressed

Eq. (3), the factor of 2 in Eq. (13) accounts for the electron spin degeneracy The chemisorption energy, ΔW, is obtained from Eq. (13) simply by integrating in t_a, from zero to t_a:

$$\Delta W = W(t_a) - W(t_a=0) =$$

$$= - \frac{2}{\pi} \int_0^{t_a} dt_a \int_0^{E_F} dE \ \mathrm{Im} \{G_{sa}(E) + G_{as}(E)\} \quad . \tag{14}$$

The t_a functional dependence of Green's function G_{as} in Eq. (14) can be made explicit by solving Dyson's equation

$$G = G^\circ + G^\circ H_{ad} \, G \quad , \tag{15}$$

where G° is the "free Green's function" corresponding to H° in Eq. (1). Dyson's equation can be exactly solved for G_{sa} using the fact that $G^\circ_{sa} = 0$, *i.e.*, atom and surface are uncoupled ($t_a = 0$) in the "free system". We obtain from Eq. (15)

$$G_{as} = G_{sa} = t_a \frac{G^\circ_{ss} \ G^\circ_{aa}}{1 - t_a^2 \, G^\circ_{ss} \ G^\circ_{aa}} \quad . \tag{16}$$

Substituting (16) into Eq. (14) and performing the t_a integration we obtain the sum rule

$$\Delta W = \frac{2}{\pi} \int_{-\infty}^{E_F} dE \ \mathrm{Im} \ \ell n \ \{1 - t_a^2 \, G^\circ_{ss} \ G^\circ_{aa}\} \quad . \tag{17}$$

Eq. (17) gives the way to sum up the series in Eq. (4). It is a exact and general equation relating the chemisorption binding energy to (i) the properties of free atoms (through G°_{aa}), (ii) the electronic properties of the clean solid surface (through G°_{ss}), properties such as bandwidth, work function, Fermi energy, etc., and (iii) to geometry of the active site in chemisorption (through the linear combination $|s\rangle$). Eq. (17) represents a great spare of effort as compared to Eq. (4), where it is required to know everything about the electronic structure of the system after and before chemisorption.

2.2 How to use Eq. (17)

There are no special directions in order to use Eq. (17). However, the long-function is a little bit tricky and some explanation is in order. The starting point is a suitable pair of Green's functions G°_{aa} and G°_{ss}. As a simple example we take chemisorption of atoms at a single site of a Bethe lattice with nearest neighbors interaction. The Hamiltonian for the free system is

$$H^{\circ} = \sum_{\langle ij\rangle} V|i\rangle\langle j| + \varepsilon_a \; |a\rangle\langle a| \tag{18}$$

and the adsorption Hamiltonian is

$$H_{ad} = t_a \left(|o\rangle\langle a| + |a\rangle\langle o|\right) \quad , \tag{19}$$

where $|o\rangle$ is the Wannier function at the site of adsorption ($i=0$), $-\varepsilon_a$ is the ionization energy of the free atom (energy is being measured from the center of the band).

The electronic structure corresponding to H°, Eq. (18), is solved in the Bethe lattice approximation. The local Green's functions we need are

$$G^{\circ}_{oo} = \begin{cases} \dfrac{(z-2)x - iz\sqrt{z-1-x^2}}{V(z^2-4x^2)} \, , & |x|<\sqrt{z-1} \\[2em] \dfrac{z-1}{V((z-2)x + \operatorname{sgn}(x) \; z\sqrt{x^2+1-z})} \, , & |x|>\sqrt{z-1} \end{cases} \tag{20}$$

and $G^\circ = 1/2V(x-\alpha)$, where $x = E/2v$, $\alpha = \varepsilon_a/2V$ and z is the coordination number of the Bethe lattice.

The energy spectrum of the free system as given by the singularities of the Green's function, consists of a continuum of states forming a band in the range $|x|<\sqrt{z-1}$ and a localized state at site a of energy $x=\alpha$. The origin of the energy axis is at the center of the band [see Eq. (18)] . The energy spectrum of the chemisorbed system is slightly different. It also has a continuum of states in the same range of values of x but the position x_o of the localized state changes deeply. The zeros of

$$f(x) = 1-t_a^2\, G^\circ_{oo}(x)\, G^\circ_{aa}(a) \tag{21}$$

give the position in energy, x_o, of the localized states. Note that f(x), defined in Eq. (21), is just the argument of the log-function in the sum rule, Eq. (17).

There are four different cases concerning the zeros of f(x) depending on the values of α and $\gamma \equiv t_a/V$. The broken lines in Fig. 1.b are the border lines in the γ-α plane separating those four cases. For values of (α,γ) within the shaded region of Fig. 1.b f(x) has two zeros corresponding to two localized states, one below and one above the band. There are no localized states for values of α and γ contained in the region of Fig. 1.b marked with a star. The unmarked region corresponds to one localized state above the band and the region containing the dot corresponds to one localized state below the band.

After these preliminaries we proceed to calculate ΔW. Let us begin with the case of a localized state below the band. From the definition of f(x) in Eq. (21), it has the following properties:

$$f(x) \to 1 \quad \text{as} \quad |x| \to \infty \,,$$

$$\text{Im } f(x)=0 \quad \text{for} \quad |x|>\sqrt{z-1} \quad ,$$

$$\text{Re } f(x_o) = f(x_o) \quad , \quad \text{for} \quad |x_o|>\sqrt{z-1} \,.$$

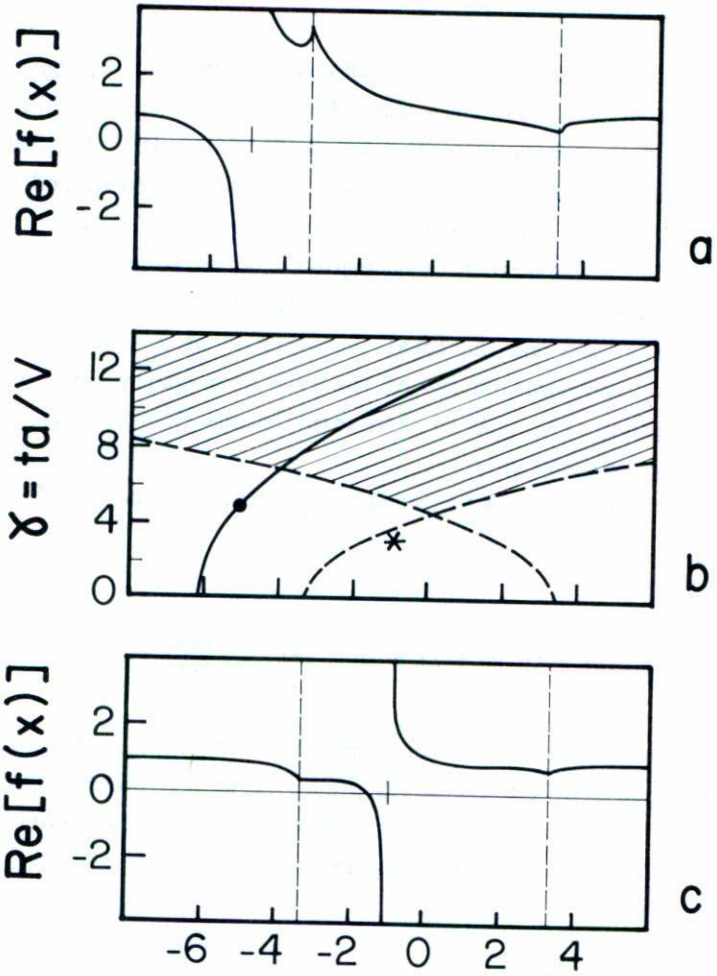

Fig. 1. (a) Plot of the real part of f(x), as defined in Eq. (21), for $\alpha= -5$ and $\gamma=5$. The broken lines mark the bandedges. The tick crossing the abscissas axis is at $x=\alpha$ where Re(f) changes sign through infinity. Re(f) changes sign through zero at $x=x_o=-6.118$.

(b) the dashed lines border four different regions on the α-γ plane concernig the roots of f(x). For values of α and γ on the shaded region there are two localized states, one at each side of the band. No localized states appear for values within the region marked with a star. Values within the unmarked region correspond to one localized state above the band. One localized state appears below the band for values of α and γ in the fourth region marked by a dot. A localized state at x = -6.118 appears for any pair of values of α and γ along the full line.

(c) Plot of the real part of f(x), as defined in Eq.(21), for $\alpha=-1$ and $\gamma=3$. The dashed lines mark the band edges. The tick corssing the abscissas axis is at $x=\alpha$ and Re f=0 at $x=y_o$.

The function $f(x)$ is purely real outside the band and changes sign twice, at $x=x_o$ and at $x=\alpha$. Fig. 1.a shows Re $f(x)$ for $\alpha=-5$ and $\gamma=5$. These values of α and γ correspond to the dot in Fig.1.b. For all values of α and γ along the full line in Fig.1.b there is always a localized state at $x_o=-6.118$. Note that the line sets up precisely at this values of α when $\gamma=0$, *i.e.*, when the system is uncoupled $x_o=\alpha$ as it must be for the free atom. The dashed lines in Fig.1.a are the band edges, the tick on the $f=0$ axis is at $x=\alpha$ and the localized state is at $x_o=-6.118$, *i.e.*, $f(x_o)=0$. Observe that the position $x=\alpha$ of the free atom energy level is shifted to lower energies, $x=x_o$, due to chemisorption and that Re $f(x)$, is negative in the range $x_o<x<\alpha$ only.

To calculate ΔW we found useful to write the log-function in the form

$$\ell n\ f(x) = \ell n\ \mathrm{Re}\ f(x) + \ell n \left(1+i\ \frac{\mathrm{Im}\ f(x)}{\mathrm{Re}\ f(x)} \right) . \tag{22}$$

The argument of the second log-function on the R.H.S. of Eq.(22) stays on the R.H.S. half of the f-complex plane, so we can freely change the values of x without crossing the branch cut. The first log-function on the R.H.S. of Eq. (22) has a real argument, so

$$\mathrm{Im}\ \ell n\ \mathrm{Re}\ f(x) = \begin{cases} 0 , & \mathrm{Re}\ f(x)>o \\ (2n+1)\pi,\ n=o,\pm1,\ldots, & \mathrm{Re}\ f(x)<o \end{cases}$$

and $\mathrm{Im}\ \ell n\ f(x) = \arctan \dfrac{\mathrm{Im}\ f(x)}{\mathrm{Re}\ f(x)} + (2n+1)\pi\ \theta\left[-\mathrm{Re}\ f(x)\right]$ (23)

where $\theta(x)$ is the Heaviside function and the inverse tanget function takes values from $-\pi$ to π.

Note that the first term on the R.H.S. of Eq. (23) vanishes for values of x outside the band ($|x| >\sqrt{z-1}$) and the second one is different from zero for values of x such that $x_o<x<\alpha$ (see Fig.1.a), where Re $f(x)<o$.

Using Eqs. (23) and (17) we obtain

$$\Delta W = 2(E_o-\varepsilon_a) + \frac{2}{\pi}\int_{-E_1}^{E_F} dE \ \mathrm{Im}\ \ell n\ \{1-t_a^2\ G_{oo}^2\ G_{aa}^2\} \quad , \tag{24}$$

where $E_o = 2Vx_o$ and $E_1 = 2V\sqrt{z-1}$. The edges of the band are at $E = \pm E_1$. The infinite many Riemann sheets of the log-function in the f-complex plane were labeled by integer n, as shown in Eq. (23). The value n=0 was used to write Eq. (26) in order to have $\Delta W(E_F = E_1) = 0$, *i.e.*, the binding energy must be zero when all the electronic states are filled. This is a very general feature that stems from the non-diagonal character of H_{ad}. Indeed, when all the states are occupied, the change in total energy is

$$\Delta W = \mathrm{Tr}\ H^\circ - \mathrm{Tr}\ H = \mathrm{Tr}\ H_{ad} = 0 \quad . \tag{25}$$

In Fig. 2 ΔW is given as a function of Fermi energy by the full line. It corresponds to $\alpha = -5$ and $\gamma = 5$, values shown by the dot in Fig. 1.b.

We conclude this section showing the calculation for the case that there are no localized states in the spectrum. Fig. 1.c shows Re f(x) for $\alpha = -1$ and $\gamma = 3$. These values correspond to the star in Fig. 1.b.

An analysis of the imaginary part of log-function similar to that we made before yields

$$\Delta W = \frac{2}{\pi}\int_{-E_1}^{E} dE \ \arctan\frac{\mathrm{Im}\ f(x)}{\mathrm{Re}\ f(x)} + \begin{cases} C & \text{if } E_F<E_o \\ 2(E_o-E_F) & \text{if } E_o<E<\varepsilon_a \\ 2(E_o-\varepsilon_a) & \text{if } E_F>\varepsilon_a \end{cases} \quad , \tag{26}$$

where E_o is now given by $E_o = 2Vy_o$, t_o being the zero of Ref(x) (see Fig.

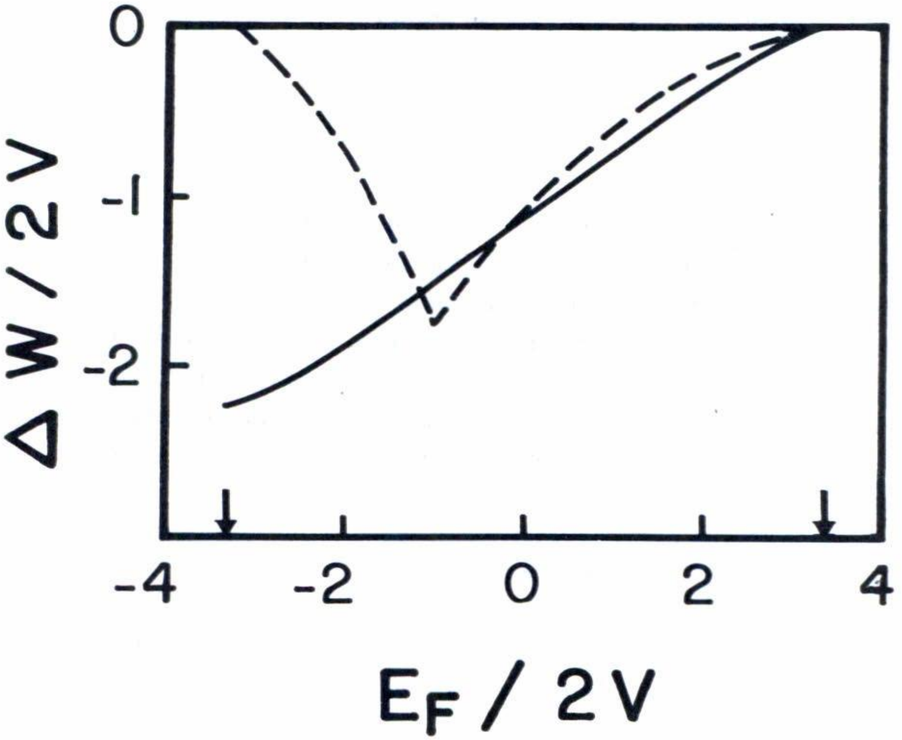

Fig. 2 $\Delta W/2V$ as a function of $E_F/2V$. The full line corresponds to $\alpha = -5$ and $\gamma = 5$ (these values of α and γ are shown as a dot in Fig.1.b). The dashed line corresponds to $\alpha = -1$ and $\gamma = 3$ (shown by the star in Fig.1.b).

1.c). Ref(x) is a different function that f(x) [see Eq. (20)], *i.e.*, x_0 and y_0 are zeros of different functions. The dashed line in Fig.2 shows how ΔW as given by Eq. (26) behaves as a function of the Fermi energy. This dashed line corresponds to the star in Fig.1.b having the values $\alpha = -1$ and $\gamma = 3$.

3. DISCUSSION AND CONCLUSIONS

We have derived an exact sum rule for the binding energy of chemisorption of atoms and illustrated its use with a very simple one-band model describing the metallic surface, namely, adsorption at a single site of a Bethe lattice [see Eqs. (18), (19) and (20)]. The important parameters in the model are $\alpha = \varepsilon_a/2V$ (*i.e.* the ionization energy of the adatom as measured from the center of the band in units of 2V) and the ratio $\gamma = t_a/V$. Fig. 2 shows the resulting binding energies as a function of $E_F/2V$ (the arrows mark the band edges) for two different sets of values of α and γ. The full line corresponds to $\alpha = -5$ and $\gamma = 5$ (see Fig. 1.a and 1.b), when a localized state is present below the band in the energy spectrum. In this case, the adatom binds more strongly to the surface when the band is almost empty and ΔW grows up monotonically to zero at the top of the band. ΔW vanishes for a filled band due to the non-diagonal character of H_{ad}. Indeed, when all states are occupied the binding energy is given by $\mathrm{Tr}\, H_{ad} = 0$. Fig. 3 shows data for the binding energy of chemisorption (rigth hand scale) of hydrogen on 3d (circles) and 4d (squares) transition metal surfaces. It can be seen there that ΔW fails to vanish when the number of d electrons is almost 10 (*i.e.* Ni and Pd). The same behavior is observed$^{(1)}$ for adsorption of O_2, CO, CO_2 and N_2. We think this fact is an indication that there is a relatively large fraction of electronic states still empty above the Fermi energy so that Eq. (25) does not hold for Ni and Pd. This could be atributed to the admixture of sp- and d-states in transition metals.

The full line in Fig.3 is the binding energy (left hand scale) as a function of the number of d- electrons N_d as given by our oversimplified model. The parameters were held constant at $V=1$, $\alpha = -5$ and $\gamma = 5$ for all values of N_d. Note that the energy scales for the theoretical prediction and data were arbitrarily shifted by 0.7eV so as to make the line go through the data. We expect this shift will be produced by the mixing of sp and d-states in a realistic model.

The dashed line in Fig.2 shows ΔW as a function of $E_F/2V$ for $\alpha = -1$ and $\gamma = 3$ (see Figs. 1.b and 1.c), that is the case when no localized state exists in the energy spectrum. The binding energy shows a sharp deep when the Fermi energy lies near the value of α and vanishes at both edges of the band. The absence of such a deep in the observed trends for adsorption of simple gases on transition metal surface announces the presence of a localized state below the d-band. Such a state has already been observed by angle-resolved photoelectron spectroscopy of hydrogen

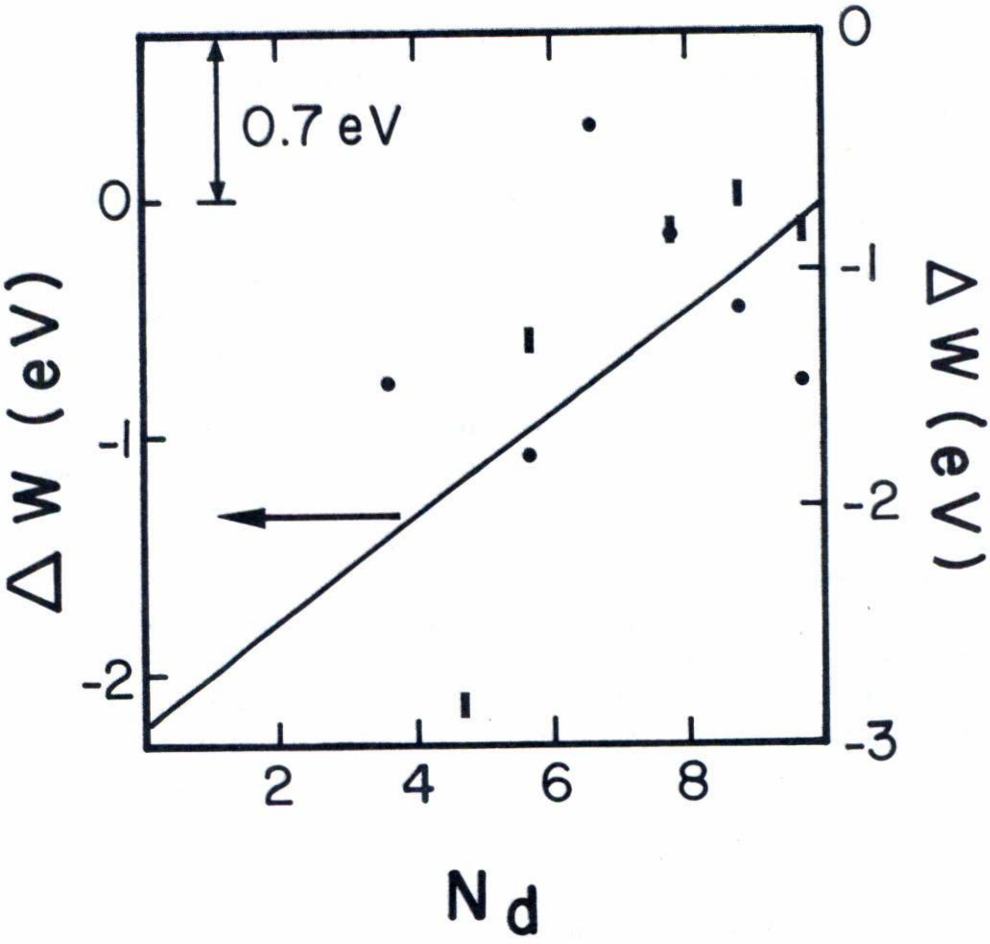

Fig. 3. Binding energy of chemisorption as a function of the number of d- electrons N_d. The displayed data are for H_2 on 3_d (circles) and 4d (squares) transition metal surfaces, as reported by Toyoshima and Somorjai (1979). The energy axis for the data is the one at the right hand side. Shifted downwards by 0.7 eV on the left hand side is the energy axis for the theoretical prediction (full line). We used $\alpha = -5$, $\gamma = 5$ and $V = 1$, the same for all N_d values.

adsorbed on Ni, Pd and Pt$^{(9)}$.

In conclusion, we have discussed the derivation of a sum rule, Eq. (17), for the binding energy of chemisorption, ΔW, and adopting a highly simplified and unrealistic model (it does not include d-d correlation effects$^{(10,11)}$ which are very important in transition metals and the metallic surface was replaced by a Bethe lattice) its use was illustrated. The sum rule can be extended to treat chemisorption of molecules and/or to include some other electronic properties of the solid surface, *e.g.*, self-consistency effects, ferromagnetism and admixture of sp- and d-states. Finally, it is worth to emphasize that the sum rule is an efficient way relating the binding energy of chemisorption to the electronic properties of the clean surface, the geometry of the chemisorption site and the adatom parameters.

ACKNOWLEDGMENTS

This work was supported in part by D.G.I.C. y S.A. de la S.E.P. (MEXICO) and by Programa Regional de Desarrollo Científico y Tecnológico de la OEA.

REFERENCES

1. I. Toyoshima and G.A. Somorjai, *Catal.Rev. Sci. Eng.* 19 (1979) 105.
2. T.L. Einstein, J.A. Hertz and J.R. Schrieffer, *Theory of Chemisorption* Springer-Verlag, Berlin (1980) pp 183-235.
3. T.L. Einstein and J.R. Schrieffer, *Phys. Rev.* B7 (1973) 3629.
4. P. Villaseñor-González, J. Urías, F. Mejía-Lira, *Phys. Rev.* B26 (1982) 7070.
5. G. Toulouse, *Solid State Comm.* 4 (1966) 593.
6. J.L. Morán-López and L. Falicov, *Phys. Rev.* B26 (1982) 2560.
7. C.M. Varma, A.J. Wilson, *Phys. Rev.* B22 (1980) 3795; *Phys. Rev.* B22 (1980) 3805.
8. R.P. Feynman, *Phys. Rev.* 56 (1939) 340.
9. W. Eberhardt, F. Greuter and E.W. Plummer, *Phys. Rev. Lett.* 46 (1981) 1085.
10. M.C. Gutzwiller, *Phys. Rev.* 134A (1964) 923.
11. J. Kanamori, *Prog. Theor. Phys.* 30 (1963) 275.