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V. I. OSHEROV

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Abstract

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V. I. OSHEROV

ON THE EFFECT OF THE MUTUAL INFLUENCE OF ADSORBED PARTICLES

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The effect of the mutual influence of chemisorbed particles (atoms, molecules) (^1) should naturally be associated with the delocalization of the electron wave functions in the adsorbent crystal, leading to the appearance, between particles, of a repulsion that decreases with distance Δ substantially more slowly than $e^{-\Delta/a_0}$ (a_0 is the Bohr radius).

To consider the dependence of the differential heats of adsorption on the degree of surface coverage—one of the manifestations of the mutual-influence effect—we shall use the method of localized states in molecules and crystals ([2,3]) as applied to adsorption (^4). The results are a development of those obtained earlier by another method (^5).

Let us introduce the following notation:

$$H_1 = H_0 + V_1 \tag{1}$$

the Hamiltonian of an electron in a crystal in the one-electron approximation (H_0 is the kinetic energy, V_1 is the average potential in the crystal);

$$H_2 = H_0 + V_2 \tag{2}$$

the Hamiltonian of an electron in a layer of chemisorbed atoms without taking into account their interaction with the adsorbent (V_2 is the potential of the atomic cores);

$$H = H_0 + V_1 + V_2 \tag{3}$$

the Hamiltonian of an electron in the adsorbate-adsorbent system. The corresponding eigenvalues and eigenfunctions are: $\varepsilon_k^j, \varepsilon_0$ (neglecting the interaction $e^{-\Delta/a_0}$), ε; $|k,j\rangle$, $\sum_m d_m|a_{2m}\rangle$, $|l\rangle$ (k is the quasi-momentum in band j; m is the position of the adsorbed atom on the surface).

Let

$$|l\rangle = \sum_{k,j} c^j_{1k}|k,j\rangle + \sum_m c_{2m}|a_{2m}\rangle. \tag{4}$$

Then, putting $\langle k,j|a_{2m}\rangle = 0$, we obtain

$$c^j_{1k} = \sum_{k',j'} c^{j'}_{1k'} \frac{\langle k,j|V_2|k',j'\rangle}{\varepsilon - \varepsilon^j_k} + \sum_m c_{2m} \frac{\langle k,j|V_1|a_{2m}\rangle}{\varepsilon - \varepsilon^j_k},$$

$$c_{2m} = \sum_{m'} c_{2m'} \frac{\langle a_{2m}|V_1|a_{2m'}\rangle}{\varepsilon - \varepsilon_0} + \sum_{k,j} c^j_{1k} \frac{\langle a_{2m}|V_2|k,j\rangle}{\varepsilon - \varepsilon_0}. \tag{5}$$

A Fourier transformation with respect to the quasi-momentum k of each band j, corresponding to the transition to a description of the crystal by Wannier functions (^4),

gives

$$c^j_{1\mathbf{n}} = \sum_{n',\mathbf{n}'',j'} c^{j'}_{1\mathbf{n}'}\langle a^j_{1\mathbf{n}''}|V_2|a^{j'}_{1\mathbf{n}'}\rangle I^j_{n''-\mathbf{n}} + \sum_{m,\mathbf{n}'} c_{2\mathbf{m}}\langle a^j_{1\mathbf{n}'}|V_1|a_{2\mathbf{m}}\rangle I^j_{n'-\mathbf{n}},$$

$$c_{2\mathbf{m}} = \sum_{m'} c_{2\mathbf{m}'}\langle a_{2\mathbf{m}}|V_1|a_{2\mathbf{m}'}\rangle \frac{1}{\varepsilon - \varepsilon_0} + \sum_{n,j} c^j_{1\mathbf{n}}\langle a_{2\mathbf{m}}|V_2|a^j_{1\mathbf{n}}\rangle \frac{1}{\varepsilon - \varepsilon_0}, \tag{6}$$

where $c^j_{1\mathbf{n}}$ and $a^j_{1\mathbf{n}}$ are the Fourier transforms of $c^j_{1\mathbf{k}}$ and $|\mathbf{k},j\rangle$,

$$I^j_{n'-\mathbf{n}} = \frac{1}{N}\sum_k \frac{e^{i\mathbf{k}(\mathbf{n}'-\mathbf{n})}}{\varepsilon - \varepsilon^j_k}, \tag{7}$$

N is the principal region of the crystal.

Let us now assume that $V_1 \sim$ const (the case of a metal) and $\langle a^j_{1\mathbf{n}}|V_2|a^{j'}_{1\mathbf{n}'}\rangle = 0$ for $j \neq j'$. Under these conditions (6) is transformed into the form

$$c^j_{1\mathbf{n}} = \sum_{n'} c^j_{1\mathbf{n}'}\langle a^j_{1\mathbf{n}'}|V_2|a^j_{1\mathbf{n}'}\rangle I^j_{n'-\mathbf{n}} + \sum_{m,\mathbf{n}'} c_{2\mathbf{m}}\langle a^j_{1\mathbf{n}'}|V_1|a_{2\mathbf{m}}\rangle I^j_{n'-\mathbf{n}},$$

$$c_{2\mathbf{m}}(\varepsilon - \varepsilon_0 - \langle a_{2\mathbf{m}}|V_1|a_{2\mathbf{m}}\rangle) = \sum_j c^j_{1\mathbf{m}}\langle a_{2\mathbf{m}}|V_2|a^j_{1\mathbf{m}}\rangle + O(e^{-\Delta/a_0}). \tag{8}$$

Restricting ourselves to the nearest neighbors of the atom numbered $\mathbf{m}$, we obtain

$$c^j_{1\mathbf{m}}(1 - \alpha^j_2 I^j_0) = c_{2\mathbf{m}}\beta^j_1 I^j_0 + \sum_{\vec{\Delta}} c^j_{1\mathbf{m}+\vec{\Delta}}\alpha^j_2 I^j_\Delta + \sum_{\vec{\Delta}} c_{2\mathbf{m}+\vec{\Delta}}\beta^j_1 I^j_\Delta + Ae^{-a/a_0},$$

$$c_{2\mathbf{m}}(\varepsilon - \varepsilon_0 - \alpha_1) = \sum_j c^j_{1\mathbf{m}} \beta^j_2. \tag{9}$$

Here the following notation has been used:

$$\alpha_1 = \langle a_{2\mathbf{m}} | V_1 | a_{2\mathbf{m}} \rangle, \qquad \beta^j_1 = \langle a^j_{1\mathbf{m}} | V_1 | a_{2\mathbf{m}} \rangle, \qquad \beta^j_2 = \langle a_{2\mathbf{m}} | V_2 | a^j_{1\mathbf{m}} \rangle. \tag{10}$$

For α^j_2 a two-sided bound can be obtained:

$$\langle a^j_{1\mathbf{m}} | V_2 | a^j_{1\mathbf{m}} \rangle < \alpha^j_2 < \frac{1}{N} \sum_k \langle \mathbf{k}, j | V_2 | \mathbf{k}, j \rangle. \tag{11}$$

The term Ae^{-a/a_0} may be discarded if a restriction is imposed on the degree of surface filling of the form $\theta > (a_0/a)^2$ (a is the lattice constant).

Assuming a sufficiently regular arrangement of the adsorbed atoms, the solution of (9) for states localized at the adsorbent surface may be sought in the form

$$c^j_{1\mathbf{m}} = C^j_1 e^{i\vec{x}\mathbf{m}}, \qquad c_{2\mathbf{m}} = C_2 e^{i\vec{x}\mathbf{m}}. \tag{12}$$

The corresponding eigenvalues are found from the equation

$$\varepsilon - \varepsilon'_0 = \sum_j z_j \frac{I^j_0 + 4I^j_\Delta \cos x_1 \cos x_2}{1 - \alpha^j_2 (I^j_0 + 4I^j_\Delta \cos x_1 \cos x_2)}; \tag{13}$$

$$I^j_0 = \frac{1}{(2\pi)^3} \int \frac{d\mathbf{k}}{\varepsilon - \varepsilon^j_k}, \qquad I^j_\Delta = \frac{1}{(2\pi)^3} \int \frac{e^{i\mathbf{k}\vec{\Delta}}}{\varepsilon - \varepsilon^j_k} \, d\mathbf{k}; \tag{14}$$

$$\varepsilon'_0 = \varepsilon_0 + \alpha_1, \qquad z_j = \beta^j_1 \beta^j_2. \tag{15}$$

In (12) and (13) x_1 and x_2 vary from $-\pi$ to π.
The solution of equation (13) can be written in the form

$$\varepsilon = \varepsilon_{\text{loc}} + f_1(\Delta, \vec{x}), \tag{16}$$

where ε_{loc}, in the first approximation, is the solution of (13) for $I^j_\Delta = 0$. The effective asymmetry of the level band (16) accounts, for the bonding states, for a finite part, of the order of the chemical bond, of the mutual-influence effect.

The other part of the effect is connected with the dependence of the position of the adsorbate bulk-state levels on the degree of filling of the surface. It can be shown that in this case the solution of (9) is sufficiently sought in the form

$$c^j_{1m} = C^j_{1k} e^{ikm}, \qquad c_{2m} = C_{2k} e^{ikm}. \tag{17}$$

Then (5)

$$\varepsilon = \varepsilon^j_k + \frac{M}{N} f^j_2(\Delta, k); \tag{18}$$

M is the number of atoms adsorbed on the principal region of the crystal,

$$f^j_2(\Delta, k) = \nabla \varepsilon^j_k \delta^j(\Delta, k). \tag{19}$$

In the case $\varepsilon^j_k = \varepsilon^j_k \delta^j(\Delta, k)$ is found from the equation

$$\varepsilon^j_k - \varepsilon'_0 = \sum_{j'} z_{j'} \frac{I_0^{j'} + 4I_\Delta^{j'} \cos k_1\Delta \cos k_2\Delta}{1 - \alpha_2^{j'} \left(I_0^{j'} + 4I_\Delta^{j'} \cos k_1\Delta \cos k_2\Delta\right)}, \tag{20}$$

in which

$$I^j_0 = \frac{1}{(2\pi)^3} \text{ v.p.} \int \frac{dk'}{\varepsilon^j_k - \varepsilon^j_{k'}} + \pi \frac{dk}{d\varepsilon^j_k} \operatorname{ctg} \pi\delta^j(\Delta, k),$$

$$I^j_\Delta = \frac{1}{(2\pi)^3} \text{ v.p.} \int \frac{e^{ik'\vec{\Delta}}}{\varepsilon^j_k - \varepsilon^j_{k'}} dk' + e^{ik\vec{\Delta}} \frac{dk}{d\varepsilon^j_k} \operatorname{ctg} \pi\delta^j(\Delta, k), \tag{21}$$

$$I_0^{j'} = \frac{1}{(2\pi)^3} \int \frac{dk'}{\varepsilon^j_k - \varepsilon^j_{k'}}, \qquad I_\Delta^{j'} = \frac{1}{(2\pi)^3} \int \frac{e^{ik'\vec{\Delta}}}{\varepsilon^j_k - \varepsilon^j_{k'}} dk'.$$

If the bands j, j' intersect in some part of k-space, then the corresponding $\delta^j(\Delta, k)$ are still found from equation (20), in which $I_0^{j'} = \infty$, $I_\Delta^{j'} = \infty$, and therefore

$$\varepsilon^j_k - \varepsilon'_0 = z_j \frac{I^j_0 + 4I^j_\Delta \cos k_1\Delta \cos k_2\Delta}{1 - \alpha^j_2 \left(I^j_0 + 4I^j_\Delta \cos k_1\Delta \cos k_2\Delta\right)} - \sum_{j' \neq j} \frac{z_{j'}}{\alpha_2^{j'}}. \tag{22}$$

Let us now take into account that the density of levels in the bulk bands (18) is significantly greater than in the surface band (16); then for the differential heats of adsorption one obtains

$$Q = Q_0 - \frac{2}{(2\pi)^2} \int f_1(\Delta, \vec{x})\, d\vec{x} - \frac{2}{(2\pi)^3} \sum_j \int f^j_2(\Delta, \mathbf{k})\, d\mathbf{k}, \tag{23}$$

where

$$Q_0 = \Phi + \varepsilon_{k_F} - \varepsilon_0 - 2\varepsilon_{\text{loc}}, \tag{24}$$

and $-\Phi$ is the interaction energy of the atomic core with the lattice core. In (23) the first integral is taken over the entire band (16), and the second up to the Fermi momentum k_F of the crystal; here the first behaves as $e^{-\Delta/a}$, and the second

as $\dfrac{\sin k_F\Delta}{\Delta}$. Both terms decrease much more slowly than ordinary repulsion $e^{-\Delta/a_0}$.

After averaging over Δ, (23) gives

$$Q = Q_0 + F_1(A_{\text{int}}, \lambda)\theta + F_2(k_F)\theta. \tag{25}$$

Here A_{int} is a combination of α_1, α_2, z; $\lambda = \left|\dfrac{\varepsilon_0 - \alpha}{2\beta}\right|$ may be called the degree of localization of the bond; α and β are the effective Coulomb and resonance integrals of the crystal; θ is the degree of surface coverage, $F_1 < 0$, $F_2 < 0$, $|F_1(\lambda)| \sim e^{-\lambda}$, $|F_2(k_F)|$ has a maximum in the middle part of the valence bands.

Already at this stage a definite comparison of the theory with experiment can be made. Thus, according to the magnitude of $dQ/d\theta$, the metals should be arranged in the following order:

$$\text{Pt} > \text{W} > \text{Ta} > \text{Pd} > \text{Ni} > \text{Co} > \text{Fe}.$$

For gases, the corresponding sequence, judging from the fraction of the dipole character of the bond, is as follows:

$$\text{N}_2 > \text{H}_2 > \text{CO} > \text{O}_2.$$

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Physical Chemistry Institute
named after L. Ya. Karpov

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.