ON THE THEORY OF CHEMICAL ADSORPTION

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Abstract

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Recently, in works on the theory of chemical adsorption ($^{1-3}$), the method of localized states in molecules and crystals (^{4,5}) has been used; this method substantially simplifies the problem of finding eigenvalues. However, a certain limitation of it makes it necessary to attempt the direct use of Bloch functions to describe the adsorbent crystal. Such an approach is already equally applicable both to metals and to dielectrics. In addition, it becomes possible to take into account in a natural way the effect of the mutual influence of adsorbed particles ($^{6-11}$).

Let us consider a system of particles adsorbed on the surface of a crystal. The one-electron Hamiltonian in the unperturbed crystal is

$$H_1 = -\frac{\hbar^2}{2m}\nabla^2 + V_1, \tag{1}$$

in the system of adsorbed particles without taking into account their interaction with the crystal,

$$H_2 = -\frac{\hbar^2}{2m}\nabla^2 + V_2, \tag{2}$$

and in the complete system adsorbate—adsorbent,

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_1 + V_2. \tag{3}$$

The corresponding eigenfunctions, in Dirac notation, are $k\rangle$, $\sum c_m m\rangle$ (c_m are determined from the requirement of the minimum of the energy H_2), $I\rangle$; k denotes both the band number and the wave vector within it; m is the position of the adsorbed particle; I denotes the new energy levels. The eigenvalues will be ε_k, ε_0 (neglecting the overlap of $m\rangle$), ε.

Let us take $I\rangle$ in the form of the linear combination

$$I\rangle = S + \alpha_k k\rangle + \sum a_m m\rangle, \tag{4}$$

where the symbol S denotes summation over band numbers and integration over momenta within them. We note that representation (4) subsequently requires exact allowance for the nonorthogonality of $k\rangle$ and $m\rangle$.

The quantities α_k and a_m are determined from the requirement of the minimum of the energy ε. The corresponding equations may be written in the form

$$\alpha_k = S\alpha_{k'}\langle k(\varepsilon - H_1)^{-1}V_2 k'\rangle + \sum a_m \langle k(\varepsilon - H_1)^{-1}(H_2 - \varepsilon + V_1)m\rangle, \tag{5}$$

$$a_m = \sum a_{m'}\langle m(\varepsilon - H_2)^{-1}V_1 m'\rangle + S\alpha_k\langle m(\varepsilon - H_2)^{-1}(H_1 - \varepsilon + V_2)k\rangle.$$

They have the following solutions

$$\begin{aligned} \alpha_k &= SR_\alpha(k,k')\sum a_m\langle k'|(\varepsilon - H_1)^{-1}(H_2 - \varepsilon + V_1)|m\rangle, \\ a_m &= \sum R_a(m,m')S\alpha_k\langle m'|(\varepsilon - H_2)^{-1}(H_1 - \varepsilon + V_2)|k\rangle. \end{aligned} \tag{6}$$

The resolvents $R_\alpha(k,k')$ and $R_a(m,m')$ are readily found through the iterated kernels $K_\alpha^n(k,k')$ and $K_a^n(m,m')$ of the basic equations (5)

$$R_\alpha(k,k') = \sum_{n=0}^{\infty} K_\alpha^n(k,k'), \qquad R_a(m,m') = \sum_{n=0}^{\infty} K_a^n(m,m'). \tag{7}$$

Taking into account the completeness of the systems $|k\rangle$ and $|m\rangle$, we obtain

$$\begin{aligned} R_\alpha(k,k') &= \langle k|[1 - (\varepsilon - H_1)^{-1}V_2]^{-1}|k'\rangle, \\ R_a(m,m') &= \langle m|[1 - (\varepsilon - H_2)^{-1}V_1]^{-1}|m'\rangle. \end{aligned} \tag{8}$$

In fact, completeness may be satisfied only approximately, which, however, does not limit the possibilities of the representation (4).

Let us now eliminate α_k from (6) and use (8); then we obtain

$$a_m = \sum a_{m'} S\langle mV_k k\rangle\langle kV_k^{-1}m'\rangle; \tag{9}$$

$$V_k = \frac{\varepsilon_k - \varepsilon + V_2}{\varepsilon_0 - \varepsilon + V_1}. \tag{10}$$

In the case of adsorption of one particle, the problem reduces to finding the roots of the equation

$$1 - S\langle mV_k k\rangle\langle kV_k^{-1}m\rangle = 0. \tag{11}$$

In the case of adsorption of many particles, however, in (9) one may use a representation in terms of the nearest neighbors of the particle with number m, which reveals the effect of mutual influence. Thus, neglecting the nonorthogonality of $|k\rangle$ and $|m\rangle$ and assuming considerable localization of the bond, we obtain

$$\varepsilon = \varepsilon_{k,0} + 4\pi n \frac{\langle mV_2 k\rangle\langle kV_1 m\rangle}{|\varepsilon_k - \varepsilon_0|}\,\theta. \tag{12}$$

Here n is the number of nearest neighbors; θ is the degree of surface coverage; $\varepsilon_{k,0}$ does not depend on θ.

The differential heats of adsorption $Q(\theta)$ are found from the relation

$$Q(\theta) = S(\varepsilon_k - \varepsilon) + \varepsilon_0, \tag{13}$$

where S refers to the occupied states.

(12) and (13) give

$$Q(\theta) = Q_0 - Zn\frac{\langle mV_2 V_1 m\rangle}{|\varepsilon_{k_0} - \varepsilon_0|}\,\theta; \tag{14}$$

Q_0 is the initial heat of adsorption; ε_{k0} is a certain mean energy in the valence band of the crystal; Z is the ratio of the volumes bounded by the Fermi surface and by the surface of the nearest Brillouin zone.

In typical cases the total decrease of the heat of adsorption, estimated from (14), is a quantity of the order of 1 eV.

Thus, even under the assumption of the absence of a direct interaction of adsorbed particles, i.e., one not dependent on the presence of the adsorbent, the mutual interaction of adsorbed pa-

particles there occurs an effect of mutual influence, caused by their chemical bond with the crystal, comparable in magnitude with the energy of chemisorption.

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