ON ONE POSSIBILITY IN THE QUANTUM THEORY OF CHEMICAL ADSORPTION

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Abstract

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ON ONE POSSIBILITY IN THE QUANTUM THEORY OF CHEMICAL ADSORPTION

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Most work on the quantum theory of chemical adsorption is devoted to the study of the levels of localized electron states (see, for example, ([1,2])). However, these levels are not directly connected with any observed effect. An important observed effect is the heat of adsorption, for which a proper theory is still lacking. An attempt to calculate heats was made in work ([3]).

The present work aims, in further development of work ([3]), to establish a definite procedure for calculating heats, which may be especially useful in the adsorption of complex atoms and molecules.

We shall consider the shift of the electronic energy of a crystal upon the formation of defects, applying a method convenient in the special case of adsorption.

Let us introduce the complete electronic wave functions Ψ_0 and Ψ, the equations for which we write in the form

$$(H_0 - E_0)\Psi_0 = 0; \tag{1}$$

$$(H_0 + \lambda V - E)\Psi = 0; \tag{2}$$

$$H_0 = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_i v_0(\mathbf{r}_i) + \frac{1}{2}\sum_{i,k}{}' \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_k|}; \tag{3}$$

$$V = \sum_i v(|\mathbf{r}_0 - \mathbf{r}_i|); \tag{4}$$

$v_0(\mathbf{r}_i)$ is the periodic potential averaged over the lattice; V is the perturbation created by the defect; the sums extend over all electrons.

We shall now make use of the relation

$$E = E_0 + \int_0^\lambda \langle \Psi' | V | \Psi \rangle \, d\lambda, \tag{5}$$

which, under the normalization $\langle\Psi'|\Psi\rangle = 1$, is an obvious consequence of the stationarity of the energy of the ground perturbed state of the system with respect to variations of the wave functions. Relation (5) in principle makes it possible to find the energy shift if $\Psi(\lambda)$ is known. We shall now use the one-electron approximation. This will considerably simplify the question, especially in the part concerning the possible localization of localized states. We shall neglect the interaction of the electrons with one another. Then

$$E = E_0 + 2\sum_i \int_0^\lambda \langle\psi_{\varepsilon_i}|v|\psi_{\varepsilon_i}\rangle\, d\lambda; \tag{6}$$

here ψ_{ε_i} are individual electron wave functions satisfying

satisfy the equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_0 + \lambda v - \varepsilon_i\right)\psi_{\varepsilon_i} = 0. \tag{7}$$

The spectrum of the corresponding unperturbed equation

$$\left(-\frac{\hbar^2}{2m} + v_0 - \varepsilon_{\mathbf{k}}\right)\psi_{\mathbf{k}} = 0 \tag{8}$$

will be restricted to the upper valence band ($\mathbf{k}$ is the wave vector within it; $\psi_{\mathbf{k}}$ are the corresponding Bloch functions).

Let us introduce into consideration the fundamental region of the lattice N; then the spectrum $\varepsilon_{\mathbf{k}}$ will become quasi-continuous, and we can write the solution of (7) in the form

$$\psi_{\varepsilon_i} = \frac{1}{1 - \lambda K_{\varepsilon_i} v}\,\psi_{\mathbf{k}}; \tag{9}$$

$$K_{\varepsilon_i} = (1 - P_{\mathbf{k}})\frac{1}{H - \varepsilon_i}. \tag{10}$$

Here $H = -\frac{\hbar^2}{2m}\nabla^2 + v_0$; $P_{\mathbf{k}}$ is the projector onto the state $\psi_{\mathbf{k}}$. In the limit as $N \to \infty$ [4]

$$\psi_{\varepsilon_i} = A\frac{1}{1 - \lambda G_{\varepsilon_i} v}\,\psi_{\mathbf{k}}. \tag{11}$$

Here A is a phase factor inessential for us; G_{ε_i} is the Green function, defined in accordance with the requirements of the radiation principle, which we shall write as an integral over the entire band

$$G_{\varepsilon_i}(\mathbf{r}-\mathbf{r}') = N\frac{2\pi i}{(2\pi)^3}\int \delta_+(\varepsilon_i-\varepsilon_{\mathbf{k}})\psi_{\mathbf{k}}(\mathbf{r})\overline{\psi}_{\mathbf{k}}(\mathbf{r}')\,d\mathbf{k}. \tag{12}$$

In the case of the local perturbation of interest to us, the wave functions ψ_{ε_i} are normalized [(5)], and therefore it is possible to use (5), (6), which gives ($\Delta E = E - E_0 \sim$ a part of the heat in the case of adsorption)

$$\Delta E = 2\sum_i \int_0^{\lambda} \left\langle \psi_{\mathbf{k}} \left| v\frac{1}{\left|1-\lambda G_{\varepsilon_i} v\right|^2} \right| \psi_{\mathbf{k}} \right\rangle d\lambda. \tag{13}$$

We shall now represent $\psi_{\mathbf{k}}(\mathbf{r})$ in the form of a Fourier expansion in Wannier functions $a_n(\mathbf{r})$, localized near the lattice sites,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{N^{1/2}}\sum_n e^{i\mathbf{k}n}a_n(\mathbf{r}). \tag{14}$$

Let us expand the operator $\frac{1}{1-\lambda G_{\varepsilon_i} v}$ in a series in λ. The term of $(p+1)$-st order in the matrix element, taking (14) into account, may be written in the form

$$\lambda^p \left\langle \psi_{\mathbf{k}} \left| v(G_{\varepsilon_i} v)^p \right| \psi_{\mathbf{k}} \right\rangle =$$

$$= \frac{\lambda^p}{N}\sum_{n,m_1,\ldots,m_p,n'} e^{i\mathbf{k}(n-n')} v_{nm_1} I_{\varepsilon_i}(m_1-m_2)\ldots I_{\varepsilon_i}(m_{p-1}-m_p)v_{m_p n'}. \tag{15}$$

Here we have introduced the Green function in the discrete space

$$I_{\varepsilon_i}(\mathbf{m}-\mathbf{m}') = \frac{2\pi i}{(2\pi)^3}\int e^{i\mathbf{k}(\mathbf{m}-\mathbf{m}')}\delta_+(\varepsilon_i-\varepsilon_{\mathbf{k}})\,d\mathbf{k}, \tag{16}$$

$$v_{nn'} = \langle a_n|v|a_{n'}\rangle. \tag{17}$$

Following (6), we shall restrict ourselves only to the largest of all the partial matrix elements $\alpha = v_{n_0\mathbf{n}_0}$; $\mathbf{n}_0$ is the point nearest to $\mathbf{r}_0$ among all $\mathbf{n}$. Then

$$\lambda^p\langle\psi_k|v(G_{\varepsilon_i}v)^p|\psi_k\rangle = \frac{\lambda^p}{N}I^p_{\varepsilon_i}(0)\alpha^{p+1}. \tag{18}$$

Summing the series thus obtained, we find

$$\left\langle \psi_k \left| v \frac{1}{|1-\lambda G_{\varepsilon_i} v|^2} \right| \psi_k \right\rangle = \frac{1}{N} \frac{\alpha}{|1-\lambda\alpha I_{\varepsilon_i}(0)|^2}. \tag{19}$$

In the same approximation, for two identical defects located at a distance R from one another,

$$\left\langle \psi_k \left| v \frac{1}{|1-\lambda G_{\varepsilon_i} v|^2} \right| \psi_k \right\rangle = \frac{2}{N}\alpha \left| \frac{1-[I_{\varepsilon_i}(0)-\cos \mathbf{k}R\, I_{\varepsilon_i}(R)]\lambda\alpha}{(1-I_{\varepsilon_i}(0)\lambda\alpha)^2 - I_{\varepsilon_i}(R)\lambda\alpha} \right|^2. \tag{20}$$

After substituting (19) into (13), we obtain ($\lambda = 1$)

$$\Delta E = \frac{2}{N} \sum_i \frac{1}{\operatorname{Im} I_{\varepsilon_i}(0)} \operatorname{arc\,tg} \frac{\alpha \operatorname{Im} I_{\varepsilon_i}(0)}{1-\alpha \operatorname{Re} I_{\varepsilon_i}(0)}, \tag{21}$$

where, in accordance with (16),

$$\operatorname{Im} I_{\varepsilon_i}(0) = \frac{1}{(2\pi)^2} \int \delta(\varepsilon_i - \varepsilon_k)\, d\mathbf{k}, \qquad \operatorname{Re} I_{\varepsilon_i}(0) = \frac{1}{(2\pi)^3} \mathrm{P} \int \frac{d\mathbf{k}}{\varepsilon_i - \varepsilon_k}. \tag{22}$$

Outside the limits of the spectrum $\operatorname{Im} I_{\varepsilon_i}(0) = 0$, so that, beginning with a certain α (in the three-dimensional case), at a definite ε

$$1 = \alpha \operatorname{Re} I_{\varepsilon_0}(0). \tag{23}$$

If we now take into account that $\operatorname{Re} I_{\varepsilon_i}(0)$ is continuous on crossing the boundary of the spectrum, it becomes clear that the energy found from (23) corresponds to the localizing boundary state ψ_g. In this case it undergoes resonance scattering

$$\psi_{\varepsilon_0} = \psi_g + N'(\varepsilon_0 - \varepsilon_g) \int \frac{\psi_k\, d\mathbf{k}}{\varepsilon_0 - \varepsilon_k}; \tag{24}$$

ε_g is the upper or lower boundary of the band, depending on the sign of α. Thus, finally, we obtain

$$\Delta E = 2(\varepsilon_0 - \varepsilon_g) + \frac{2}{(2\pi)^3} \int \frac{1}{\operatorname{Im} I_{\varepsilon_k}(0)} \operatorname{arc\,tg} \frac{\alpha \operatorname{Im} I_{\varepsilon_k}(0)}{1-\alpha \operatorname{Re} I_{\varepsilon_k}(0)}\, d\mathbf{k}; \tag{25}$$

the integral is taken up to the Fermi momentum k_F.

An analogous relation for the shift of the vibrational part of the free energy of the lattice was found by I. M. Lifshitz ([6,7]).

In the case of adsorption, within the framework of the simplest method of molecular orbitals,

$$\alpha = -\frac{z}{\varepsilon_0 - \varepsilon_2'} + \alpha_2, \tag{26}$$

where

$$z = \langle a_2|v_1|a_{1\mathbf{n}_0}\rangle\langle a_{1\mathbf{n}_0}|v_2|a_2\rangle; \quad \alpha_2 = \langle a_{1\mathbf{n}_0}|v|a_{1\mathbf{n}_0}\rangle; \quad \varepsilon_2' = \varepsilon_2 + \alpha_1, \quad \alpha_1 = \langle a_2|v_1|a_2\rangle;$$

ε_2 is the eigenvalue of the electron energy in the atom before adsorption. The indices 1 and 2 refer respectively to the lattice and to the adsorbed atom.

For $|\alpha| \ll \beta$ (β is the width of the band) $\Delta E \sim \alpha$, while for $|\alpha| \gg \beta$ it ceases to depend on α, but in this case the formation of a larger number of localized states is possible and a more delicate consideration is required. (25) also shows that in both limiting cases (an almost completely or very weakly filled band) $\Delta E \sim \varepsilon_F$.

Let us also note that, in accordance with (20), between two adsorbed atoms there exists an "interaction" which, at large distances R between them, behaves as const$/R^2$.

Thus we arrive at the important conclusion that, for calculating heats of adsorption, one may use the wave functions (11), which are essentially solutions of the Schrödinger equation for scattering and can be found with a sufficient degree of accuracy also in the adsorption of complex systems.

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REFERENCES CITED

[1] J. Koutecky, Trans. Farad. Soc., **54**, 1038 (1958).
[2] T. B. Grimley, Proc. Phys. Soc., **72**, 103 (1958).
[3] V. I. Osherov, DAN, **132**, No. 4, 884 (1960).
[4] B. S. De Witt, Phys. Rev., **103**, 1565 (1956).
[5] B. S. De Witt, Phys. Rev., **100**, 905 (1955).

[6] I. M. Lifshits, UMN, **7**, 171 (1952).
[7] I. H. Lifhic, Nuovo Cim., No. 4, 3, Suppl. X, 716 (1956).

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