

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME XII

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Preface

This volume will appear in print at about the same time as numerous scientists from many countries meet together at the Second International Congress of Catalysis, July 3 to July 9, in Paris, France. Both this meeting and the appearance of another volume of the *Advances in Catalysis* cause us to reflect on the unique nature of our field of interest. With colleagues from nearly all disciplines of the physical and life sciences, from nearly all nations and races, we find ourselves engaged in a common effort and quest for knowledge. We stand reminded that knowledge is the basic ingredient for creation of the things we may need or desire. How closely related the phenomenon of catalysis is to the *rate* at which we can create these things! As we give and exchange that knowledge which is the capacity for creation of what each of us may need or desire, perhaps we give and exchange the basic ingredient to peace on our planet itself.

P. B. W.

June, 1960

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The Wave Mechanics of the Surface Bond in Chemisorption

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I. Introduction

An important problem in surface chemistry concerns the nature of the bond formed when an atom or molecule is adsorbed onto the surface of a solid. The magnitude of the heat of adsorption provides a rough guide to the sort of interaction to be expected. If the heat is low, say ~ 5 kcal. mole⁻¹, we speak of physical adsorption and imply that the electronic structures of the solid and the adsorbate are not seriously modified when the two are in mutual interaction. If the heat is high, say, ~ 50 kcal. mole⁻¹, we speak of chemisorption and imply that a change in the electronic structures does occur. This change may be drastic, as with H₂ and the transition metals where the gas is chemisorbed as atoms, or less obvious

as with CO on Pt and Pd, where the molecule is undissociated but only the order of the carbon-oxygen bond changes in going from the free to the chemisorbed state (1).

This article is concerned with chemisorption, and our main problem is to discover how strong bonds might be formed between a solid and an adsorbate. This is a very difficult task. From the viewpoint of conventional valency theory, the solid is a giant molecule with free valence at its surface. This free valence is taken up by the adsorbate in forming the chemisorbed species, and the activity of the surface is thereby extinguished. This is, of course, an oversimplification. The surface may still have a residual activity, perhaps towards a different adsorbate, because the original free valence at the solid surface is partly transferred to the new surface composed of the chemisorbed species.

If we are to attempt a discussion of the surface bond using these concepts, we require a detailed knowledge of the electronic structures of both the chemisorbed species and the solid *with a free surface*. Granted this knowledge, we might expect to understand the surface bond in terms of the shapes and manners of occupation of the orbitals of the solid and the adsorbate. We know, however, from our experience in similar discussions of the binding of an atom in a molecule, that the concept of the valence state of the atom in the molecule is very important. The valence states of an atom are certain hypothetical excited states formed by linear superposition of the ground state and one or more excited states. Now in the solid metals the excited states are quasi-continuous from the ground state upwards. Hence, the possible valence states of the metal for chemisorption are also quasi-continuous, and this method of approach to the problem is not, therefore, very useful. It might be used for insulators, and even for semiconductors, but in general it seems better to adopt the molecular orbital approach. In this method we look at the outset for the one-electron wave functions and energies of the system—solid plus adsorbed species as a whole. In this way, the existence of quasi-continuous bands of energy levels in the solid is fed into the problem at the beginning and does not have to be faced explicitly later on. There exists a powerful mathematical technique for handling this and similar problems (2, 3), by which the solution is made to depend upon a knowledge of the electronic structures of the adsorbed species and of the solid with a free surface when interactions between them are ignored. It appears, therefore, that it will be impossible to develop a general theory of chemisorption without first treating the problem of the electronic structure of a solid with a free surface. Normally, when we speak of the electronic structure of a solid, we mean only those features which are independent of the conditions existing at any free surfaces or interfaces. In the next section we illustrate in the

simplest manner possible the new features which arise when a free surface is introduced.

II. A Solid with a Free Surface

Little theoretical work has been done on the electronic structure of a solid with a free surface. The main contributions are those of Tamm (4), Shockley (5), Goodwin (6), Artmann (7), and Koutecký (8), and the main conclusion is that, in certain circumstances, surface states may exist in the gaps between the normal bands of crystal states. In this section we investigate the problem in the simplest way. The solid is represented by a straight chain of similar atoms, and its two ends represent the free surfaces. This one-dimensional model exhibits the essential features of the problem, and the results are easily generalized to three dimensions.

Starting from one end, let the atoms in the chain be numbered 0, 1, . . . , N . Associated with each atom m we introduce an atomic orbital $\phi(r, m)$, and assume that any wave function $\psi(r)$ for the chain can be written as

$$\psi(r) = \sum_m \phi(r, m)c(m). \quad (1)$$

If \mathcal{H} is the effective one-electron Hamiltonian operator for the chain, $\psi(r)$ satisfies the equation

$$\mathcal{H}\psi = E\psi. \quad (2)$$

Substituting Equation (1) into Equation (2) and neglecting overlap between the atomic orbitals, we arrive at the usual system of linear equations

$$[E - H(m, m)]c(m) = \sum_n' H(m, n)c(n) \quad (3)$$

for the wave-function coefficients $c(m)$ and the energies E . In Equation (3) we have

$$H(m, n) = \int \phi^*(r, m)\mathcal{H}\phi(r, n) dr.$$

Now put

$$\begin{aligned} H(m, m) &= \alpha, \quad m \neq 0, \\ H(0, 0) &= \alpha', \\ H(m, m \pm 1) &= \beta, \end{aligned}$$

and neglect all other matrix elements of \mathcal{H} . Thus, we include only the resonance integral between nearest neighbors and take account of the existence of the free surface at $m = 0$ by changing the Coulomb integral from α to α' on this atom. These are the usual approximations of the "tight binding" method. Equation (3) now gives

$$(E - \alpha)c(m) = \beta[c(m+1) + c(m-1)], \quad m \neq 0, \quad (4)$$

with the boundary condition

$$(E - \alpha')c(0) = \beta c(1). \quad (5)$$

We still have to apply a boundary condition at the other end of the chain ($m = N$). If N is large, this boundary condition cannot affect the conditions near $m = 0$ in any important way, and we shall assume that $c(N) = 0$. This defines the problem as that of the electronic structure of a chain with one free end at $m = 0$. The solution is

$$c(m) = \sin(N - m)\theta, \quad m = 0, 1, \dots, N. \quad (6)$$

This satisfies the boundary condition at $m = N$. It satisfies Equation (4) if

$$E = \alpha + 2\beta \cos \theta, \quad (7)$$

and the boundary condition, Equation (5), if θ is one of the N roots of the equation

$$z + \cos \theta + \sin \theta \cot N\theta = 0, \quad (8)$$

with

$$z = (\alpha - \alpha')/\beta. \quad (9)$$

Equation (8) has at least $N - 1$ real roots. According to Equation (6), the corresponding wave functions are periodic, and if we write $E' = (E - \alpha)/2\beta$, then, according to Equation (7), the energy levels lie in the range

$$-1 < E' < 1. \quad (10)$$

These are nonlocalized states, and Equation (10) defines the familiar band of levels (width $4|\beta|$) arising from the single state $\phi(r)$ of the isolated atoms. The remaining root of Equation (8) may also be real, in which case the energy also lies in the band, and the chain has only nonlocalized states. On the other hand, if $|z| > 1 + N^{-1}$, the remaining root has θ of the form $i\xi$ or $\pi + i\xi$, with ξ real and positive. The corresponding wave functions are damped in the chain as we move away from the end atom. These are localized states associated with the free end at $m = 0$. Their energies lie outside the normal band of levels defined by Equation (10), and we shall refer to them as *end states*. A state with $\theta = i\xi$ has E' positive and will be denoted by \mathcal{O} ; a state with $\theta = \pi + i\xi$ has E' negative and will be denoted by \mathfrak{X} . From Equation (8), a \mathcal{O} state exists if

$$-z = \cosh \xi + \sinh \xi \coth N\xi,$$

and since N is large, we may take this condition as

$$-z = \exp \xi \quad (\xi > 0),$$

so that a \mathcal{O} state exists if $z < -1$. [The exact condition is $z < -(1 + N^{-1})$]. The wave function and the energy are given by

$$\begin{aligned} c(m) &= c(0) \exp(-m\xi), \\ E &= \alpha + 2\beta \cosh \xi. \end{aligned}$$

For an \mathcal{U} state, $z = \exp \xi$ if N is large, so that such a state exists if $z > 1$. The wave function and the energy are given by

$$\begin{aligned} c(m) &= c(0)(-1)^m \exp(-m\xi), \\ E &= \alpha - 2\beta \cosh \xi. \end{aligned}$$

The situation may now be summarized, assuming for definiteness that $\beta < 0$. [This would be the case if the orbitals $\phi(r)$ had the symmetry of atomic s -states.] When $z = 0$, the chain has N nonlocalized states with a band width $4|\beta|$. As z decreases (chain end electron attracting), the energies of all these states decrease (but only by small amounts, the maximum decrease being proportional to N^{-1}), until at $z = -1$ an end state of type \mathcal{O} separates below the band. There are now only $N - 1$ nonlocalized states in the band. As z decreases further, the \mathcal{O} level falls further below the bottom of the band, and its wave function becomes more and more concentrated on the end atom. As $z \rightarrow -\infty$, the wave function for the \mathcal{O} state degenerates to the atomic orbital $\phi(r, 0)$ centered on the end atom, and the wave functions for the nonlocalized states are zero on the end atom. As z increases above zero (chain end electron repelling), the energies of all the states in the band increase slightly, until at $z = 1$ an end state of type \mathcal{U} separates above the band. Its energy increases steadily with z , and its wave function becomes more concentrated on the end atom. Again, the wave function for the end state degenerates to $\phi(r, 0)$, and the amplitudes of the $N - 1$ nonlocalized states on the end atom fall to zero as $z \rightarrow \infty$.

The three-dimensional crystal can be treated by a straightforward generalization of the method outlined above (6). A simple cubic lattice is defined by three integers (m_1, m_2, m_3) , which take the values $0, 1, \dots, N$. A free $\langle 100 \rangle$ surface is defined by the plane $m_1 = 0$, and the Coulomb integral is changed from α to α' for all atoms in this plane. The wave functions are assumed to vanish on the other five surfaces of a cube. The wave function coefficients are given by

$$c(m_1 m_2 m_3) = \sin(N - m_1)\theta_1 \sin m_2\theta_2 \sin m_3\theta_3,$$

with $\theta_2 = k_2\pi/N$, $k_2 = 1, 2, \dots, N$, and $\theta_3 = k_3\pi/N$, $k_3 = 1, 2, \dots, N$, while θ_1 is one of the N roots of Equation (8). The energy levels are given by

$$E = \alpha + 2\beta(\cos \theta_1 + \cos \theta_2 + \cos \theta_3).$$

The essential features of the one-dimensional problem are therefore re-

tained. The only difference is that the discrete end state which exists in the one-dimensional case when $|z| > 1$ now appears as a *band of surface states* of width $8|\beta|$ and containing N^2 levels. N^2 levels are, of course, missing from the normal band of crystal states. If $|z|$ is not too large, the surface band overlaps the normal crystal band, but when $|z|$ is large, the two bands are quite separate, and the amplitudes of the normal crystal states become vanishingly small on the surface atoms. This situation is interesting because it means that as far as its external interactions are concerned, the crystal behaves like a two-dimensional array of atoms whose electronic structure is described by the band of surface states.

So far we have assumed that the electronic structure of the crystal consists of one band derived, in our approximation, from a single atomic state. In general, this will not be a realistic picture. The metals, for example, have a complicated system of overlapping bands derived, in our approximation, from several atomic states. This means that more than one atomic orbital has to be associated with each crystal atom. When this is done, it turns out that even the equations for the one-dimensional crystal cannot be solved directly. However, the mathematical technique developed by Baldock (2) and Koster and Slater (3) can be applied (8) and a formal solution obtained. Even so, the question of the existence of otherwise of surface states in real crystals is difficult to answer from theoretical considerations. For the simplest metals, i.e., the alkali metals, for which a one-band model is a fair approximation, the problem is still difficult. The nature of the difficulty can be seen within the framework of our simple model. In the first place, the effective one-electron Hamiltonian operator is really different for each electron. If we overlook this complication and use some sort of mean value for this operator, the operator still contains terms representing the interaction of the considered electron with all other electrons in the crystal. The Coulomb part of this interaction acts in such a way as to reduce the effect of the perturbation introduced by the existence of a free surface. A self-consistent calculation is therefore essential, and the various parameters in our theory would have to be chosen in conformity with the results of such a calculation.

With ionic crystals, there are some rather interesting possibilities. A large part of the perturbation which a free surface introduces is associated with the change in the electrostatic environment of an ion in going from the interior to the surface. If the normally filled valence band is associated with the anions (as is the case with the alkali halides and with certain n -type semiconducting oxides), the surface perturbation acts in the direction of producing a band of surface states with its center lying above the center of the normal anion band. This anion surface band will normally be completely filled. Conversely, for the normally empty cation band (the

conduction band) the surface perturbation acts in the direction of producing a surface cation band with its center lying below the normal cation band. Thus, the surface electronic structure shows a narrower gap between filled and vacant bands than that characteristic of the bulk structure. It is possible, therefore, that there is an intrinsic surface semiconductivity or even a metallic-like surface conductivity if the surface anion and cation bands overlap each other. Correspondingly, homopolar binding will be more important in the surface region. Effects of this sort are obviously important in the theory of chemisorption; we note, however, that this simple anion-cation band picture is not adequate for the transition metal oxides.

III. The Molecular Orbital Theory of the Surface Bond

The basic problem in the molecular orbital theory of chemisorption is to find the one-electron wave functions (molecular orbitals) and energy levels for the whole system—solid plus adsorbed species. Knowing these, we could then calculate the energy of chemisorption. So far, the theory has not been taken to the stage of an energy calculation for even the simplest case of practical interest. Enough is now known, however, about the general problem to enable a review to be given of the types of surface bonds which can arise, although little is known about the nature of the surface bond in individual cases.

We begin by considering a one-dimensional model in which the crystal is represented by a straight chain of similar atoms and a foreign atom is in interaction with one end of the chain. This is the simplest model of the chemisorption process which may be expected to yield useful results (9). If the normal electronic structure of the chain consists of just one band, this one-dimensional model is easily treated in the "tight-binding" approximation.

A. THE ONE-DIMENSIONAL MODEL

Let the atoms in the chain be numbered $0, 1, \dots, N$, and let the foreign atom be denoted by λ (Fig. 1). Associated with each atom we introduce an atomic orbital $\phi(r, m)$. These orbitals are divided into two sets. One set ($m = \lambda$) contains only one member, which is the orbital on the foreign atom; the other set ($m = 0, 1, \dots, N$) consists of the orbitals on the "crystal" atoms. Thus, we have the problem of the interaction of a hydrogen-like atom with a crystal whose normal electronic structure consists of just one band of states.



FIG. 1. One-dimensional model for chemisorption.

Any wave function for the system is expressed as

$$\psi(r) = \sum_m \phi(r, m) c(m),$$

and neglecting overlap between the atomic orbitals, we arrive at a system of linear equations like those in Equation (3), except that \mathcal{H} is now the one-electron Hamiltonian operator for the whole system, chain plus foreign atom. We make the same assumptions about the matrix elements of \mathcal{H} that we made in Sec. II, and in addition we put

$$H(\lambda, \lambda) = \alpha'', H(0, \lambda) = H(\lambda, 0) = \beta'.$$

Thus, the foreign atom is characterized by having a different Coulomb integral α'' from the crystal atoms, and we take account of its presence at the end of the chain by changing α to α' on the end crystal atom ($m = 0$), and by changing β to β' between the foreign atom and the end crystal atom. We now have Equation (4) to solve with the boundary conditions

$$\begin{aligned} (E - \alpha')c(0) &= \beta c(1) + \beta' c(\lambda), \\ (E - \alpha'')c(\lambda) &= \beta' c(0). \end{aligned}$$

As in Sec. II, we assume that the wave functions vanish at the end of the chain ($m = N$) remote from the foreign atom. If N is large, this boundary condition cannot affect the conditions near $m = 0$ in any important way. Introducing the dimensionless quantities

$$z = (\alpha - \alpha')/\beta, z' = (\alpha - \alpha'')/\beta, \eta = \beta'/\beta, E' = (E - \alpha)/2\beta$$

gives the solution

$$\left. \begin{aligned} c(m) &= \sin(N - m)\theta, m \neq \lambda, \\ c(\lambda) &= \eta \sin N\theta / (z' + 2 \cos \theta). \end{aligned} \right\} \quad (11)$$

The energy levels are given by

$$E' = \cos \theta,$$

and θ is one of the $N + 1$ roots of the equation

$$(z + \cos \theta + \sin \theta \cot N\theta)(z' + 2 \cos \theta) = \eta^2. \quad (12)$$

Equation (12) has at least $N - 1$ real roots. The corresponding wave functions are nonlocalized, and the energies lie in the range defined by Equation (10). This is the normal band of crystal states. The remaining two roots may both be real, and in this case they also lie in the normal crystal band, and the system has only nonlocalized states. On the other hand, one or both of the remaining roots may have values of θ of the form $i\xi$ or $\pi + i\xi$ with ξ real and positive. The corresponding wave functions

are damped in the crystal. These are localized states associated with the foreign atom and the crystal atoms near the "surface." Their energies lie outside the normal band of crystal states, and their existence allows for the formation of localized covalent bonds between the foreign atom and the crystal. Again we denote localized states by \mathcal{O} or \mathcal{N} according to whether E' is positive or negative. When N is large, the eigenvalue condition, Equation (12) for \mathcal{O} states is

$$(z + \exp \xi)(z' + 2 \cosh \xi) = \eta^2, \quad (13)$$

and the wave-function coefficients are given by

$$\left. \begin{aligned} c(m) &= \exp(-m\xi), \quad m \neq \lambda, \\ c(\lambda) &= \eta/(z' + 2 \cosh \xi), \end{aligned} \right\} \quad (14)$$

and the energy by $E' = \cosh \xi$. For \mathcal{N} states, the corresponding equations are

$$(z - \exp \xi)(z' - 2 \cosh \xi) = \eta^2, \quad (15)$$

$$\left. \begin{aligned} c(m) &= (-1)^m \exp(-m\xi), \quad m \neq \lambda, \\ c(\lambda) &= \eta/(z' - 2 \cosh \xi), \end{aligned} \right\} \quad (16)$$

with $E' = -\cosh \xi$. The wave-function coefficients given by Equations (14) and (16) are not normalized.

We now investigate how the occurrence of localized states is governed by the values of the parameters z , z' , and η which define the interaction between the foreign atom and the crystal. Localized states exist if either one or both of Equations (13) and (15) have real roots ξ . Real roots exist for given η in regions of the zz' -plane defined by the two hyperbolas

$$(z \pm 1)(z' \pm 2) = \eta^2. \quad (17)$$

These are plotted in Fig. 2 for $\eta^2 = 1$. Localized states occur in the six regions indicated. \mathcal{O}^2 means that there are two \mathcal{O} states, $\mathcal{O}\mathcal{N}$ that there is one \mathcal{O} state and one \mathcal{N} state, and so forth. We see that the system may have two or one or no localized states. The area of the region where there are no localized states decreases as η^2 increases, and such a "forbidden region" exists only if $\eta^2 < 2$.

The maximum number of localized states which can be formed is two. This result depends on our assumptions that only one orbital on the foreign atom and only one band of crystal orbitals are in interaction and that the perturbation of the crystal by the foreign atom does not extend beyond the first crystal atom. If we extend the perturbation (i.e., modify the Coulomb integrals) to the first and second crystal atoms, we find a maximum of three localized states. In general, the maximum number of localized states

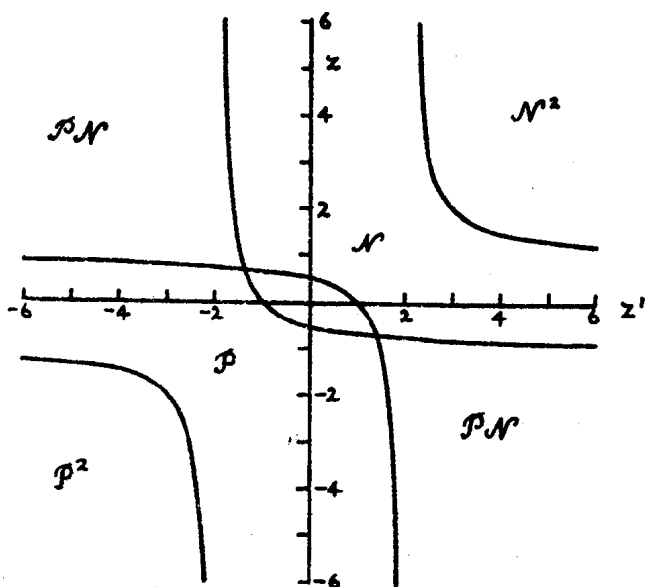


Fig. 2. The occurrence of localized states for $\eta^2 = 1$.

is equal to the sum of the number of orbitals on the foreign atom, the number of crystal atoms perturbed, and the number of bands of crystal states. Thus, the theory allows for the formation of surface bonds with multiple-bond orders. It is clear, therefore, that the simple one-dimensional model contains many features of the general chemisorption problem, and because of this, it merits a rather full discussion. Before doing this we consider briefly the generalization to a three-dimensional crystal.

B. THREE-DIMENSIONAL CRYSTAL

When we consider the interaction of a foreign atom with the free surface of a three-dimensional crystal, it turns out that the difference equation [Equation (4)] and the corresponding boundary conditions cannot be solved directly. However, the technique developed by Baldock (2) and Koster and Slater (3) is applicable (9, 10, 11). To use this method, we need the one-electron wave functions and energy levels of the crystal with a free surface, this free surface being the one at which chemisorption is to take place. As we have already indicated in Sec. II, our knowledge of these quantities is very inadequate, and if we are to proceed very far with the chemisorption problem, we are committed, more or less, to the "tight-binding" approximation once again. This is a poor approximation for all metals.

Results obtained (9) by applying this method show that, if the pertur-