

Nature of Bonds in Chemisorption on Supported Metals

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A quantum-mechanical method is used to obtain information about the nature of bonds in chemisorption on supported metals. The calculations are based on an unidimensional model composed of a finite chain of metal atoms and a semi-infinite chain of support. The linear combination of atomic orbitals and the tight-binding approximation are used to construct the wave function of one electron in the field of the chain of metal atoms, support and chemisorbed atom.

The support affects the chemisorption process, modifying the nonlocalized volume states (states with periodic wave function) and the localized states (states with non-periodic wave function); also generating new types of states in which the wave function is periodic in one layer and nonperiodic in the other (composite states). For instance, a single component finite chain of metal atoms (without support) has a single band for the volume states; with an AB-type support, the complete system can have two bands, one band or no band. The localized states can be localized at the adatom-metal surface, and/or at the metal-support interface. Also, depending upon the number of metal atoms in the chain and the nature of the support, the bond due to a localized state can change from anionic to cationic. For a composite state having wave function coefficients larger in the layer which has a periodic wave function, the electron will belong to that whole layer.

1. INTRODUCTION

The distinction between physical adsorption and chemisorption is based upon the forces involved. In physical adsorption, the forces are similar to those responsible for the liquefaction of inert gases, while chemisorption implies a "chemical bond." Two points of view have been formulated concerning the nature of the chemisorption bond. In the first, one considers a bond with the metal as a whole, in the second, one considers a bond generating a chemical compound with only some metal atoms of the interface. Comparing the heats of chemisorption of different gases on different solids and the heats of formation of bulk solids, Sachtler (*1*) noticed that they show the same trend: the heats of chemisorption are greater for greater heats of formation. From this observation, the useful conclusion was reached that a "chemical compound" is formed between the chemisorbed gas and the metal atoms of

the surface. It is, however, important to note that the surface compound does not necessarily have the same properties as a bulk solid of similar chemical composition; the heats of chemisorption appear to be always greater. Consequently, it appears that a chemical compound is formed on the surface, but this compound interacts in an important manner with the bulk of the metal. It is natural to conclude that the chemisorption bond cannot be restricted to one of the two limiting situations suggested by the "chemical" or "physical" intuition, but is a combination of both.

The first theoretical approach to the problem has considered that the bonds on a metal surface are not too different from those acting within the bulk of the metal. However, in the quantum-mechanical treatment of a solid having a free surface, special states occur (Tamm surface states) and, consequently, one may expect a similar,

more complicated, behavior when a chemisorbed layer is formed at the interface. Such an approach to the problem was developed by Koutecky (2), Grimley (3), Davison and Cheng (4), and others (5-9). Most of the work is based on a unidimensional semi-infinite chain of metal atoms having a chemisorbed atom (adatom) at one end. The LCAO (linear combination of atomic orbitals) approximation is used to construct the wave function of one electron in the field of the chain of metal atoms plus adatom. The energy levels, as well as the coefficients of the atomic wave function, are determined using a variational method and the tight-binding approximation which takes into account resonance integrals, but neglects overlap integrals. If the wave function decays inside the crystal, the electron is localized at the adatom-metal surface (localized states). If the wave function has a periodic shape, the electron belongs to the whole system (nonlocalized volume states). Depending upon the values of the interaction parameters between the metal atoms and between the adatom and metal, the localized states can lead to homopolar or ionic bonds. The nonlocalized volume states lead to metallic bonds.

For supported metal catalysts, the problem is more complex. The experimental evidence appears to show that there are two classes of reactions: in the first, the specific activity of the catalyst (defined as the rate per unit exposed area of metal) is independent of the crystallite sizes; in the second, it depends on the crystallite sizes. Several types of size dependencies have been reported in the literature (10-18).

Concerning the supported metal catalysts, two questions can be raised, namely: (a) what is the effect of the size of the crystallite upon the chemisorption bond? and (b) what is the effect of the interaction between the support and metal upon the chemisorption bond? Some answers to these questions were obtained in this study on the basis of a quantum-mechanical approach similar to that used previously for the chemisorption on a semi-infinite metal. The main conclusions are: (a) The presence of the support affects the range of parameters in which

various types of localized states exist, and also the nature of the corresponding bonds. For instance, depending upon the thickness of the crystallites, a bond due to a localized state can change from homopolar to ionic, or from anionic to cationic. The localized states can be localized at the adatom-metal surface, and/or at the metal-support interface. (b) The presence of the support has a strong effect on the number of bands for the volume states. For instance, a single component finite chain of metal atoms (without support) has a single band; with an AB-type support, the complete system can have two bands, one band or no band. (c) Composite states with a periodic wave function in one of the layers and nonperiodic wave function in the other can occur.

METHODS AND RESULTS

1. Chemisorption Model and Basic Equations

For simplicity, a one-dimensional model is considered (Fig. 1). It consists of a linear chain composed of a finite number of atoms of a pure metal or of an alloy supported on a semi-infinite substrate (an oxide for instance). For purposes of illustration, the alloy is considered as a combination of the type A_iB_j (i and j can be any positive integer; here we take $i = 1$ and $j = 1$ for convenience in the calculation) and the oxide as a compound of the form AB; an adatom is in interaction with one end of the chain, say A' metal atom. The atoms in the chain are numbered $0, 1, \dots, N$, and the adatom is denoted by λ . Associated with each atom n is an atomic orbital Φ_n . The wave function Ψ of a single electron in the system is expressed as a linear combination of the atomic orbitals Φ_n , in the form

$$\Psi = \sum_n c_n \Phi_n. \quad (1)$$

The coefficients c_n are determined by using a variational method. The wave function Ψ satisfies the one-electron Schrodinger equation,

$$H\Psi = E\Psi, \quad (2)$$

where H is the effective one-electron Hamiltonian operator for the whole system, chain

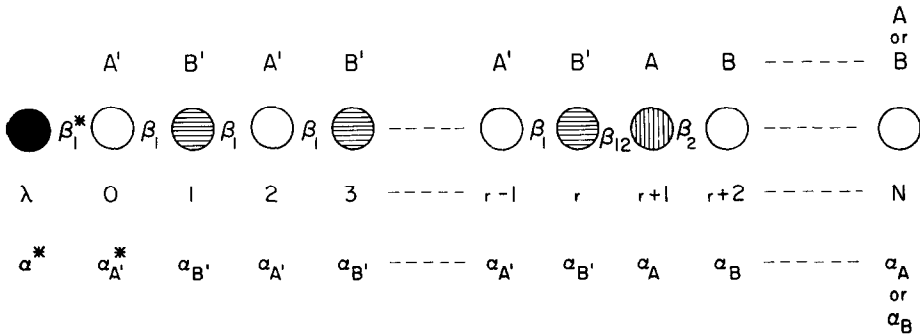


FIG. 1. Model for an adatom interaction with a finite A'B'-type metal supported on a semi-infinite AB-type oxide.

plus adatom (the interaction between electrons is neglected), and E is the corresponding electron energy. Substituting Eq. (1) into Eq. (2), multiplying through on the left by Φ_m^* and integrating over all space, one obtains the system of equations

$$\sum_n (H_{mn} - ES_{mn})c_n = 0, \quad (3)$$

where

$$H_{mn} = \int \Phi_m^* H \Phi_n d\tau, \quad (4)$$

and

$$S_{mn} = \int \Phi_m^* \Phi_n d\tau. \quad (5)$$

Assuming $\{\Phi_n\}$ form an orthonormal set, so that $S_{mn} = \delta_{mn}$, then Eq. (3) becomes

$$[E - H_{nn}]c_n = \sum_{m \neq n} H_{mn}c_m. \quad (6)$$

If the atomic orbitals Φ_n are sufficiently localized on the atom n , the Hamiltonian matrix elements H_{mn} are negligibly small for m too different from n . According to the tight-binding approximation, H_{mn} is different from zero only for $m = n$ and $m = n \pm 1$. Because H_{mn} is symmetrical in m and n , it follows that $H_{n\pm 1, n}$ has the same value whether n is odd or even. The values of $H_{n\pm 1, n}$ are denoted by β_1 and β_2 for the atoms of metal and of substrate, respectively. Because we consider an alloy of type A'B', where the atoms A' are in the even positions and the atoms B' in the odd positions, we have two values for H_{ss} :

$$\begin{cases} H_{ss} = \alpha_{A'}, & s \text{ even (A' atom)}, \\ & 0 \leq s \leq r \\ H_{ss} = \alpha_{B'}, & s \text{ odd (B' atom)}. \end{cases} \quad (7)$$

where $r + 1$ is the number of metal alloy atoms. Similarly, for the substrate we denote

$$\begin{cases} H_{mm} = \alpha_A, & m \text{ even (A atom)}, \\ & r + 1 \leq m \leq N \\ H_{mm} = \alpha_B, & m \text{ odd (B atom)}. \end{cases} \quad (8)$$

The quantities β_i and α_i are the resonance integrals and the Coulomb integrals, respectively. Physically, the α 's represent the effective energy of an electron in an atomic orbital, and the β 's the bond energy between the nearest-neighbor atoms. The tight-binding approximation reduces the complexity of Eqs. (6), which now become a set of second order difference equations with constant coefficients of the form:

$$\begin{cases} (E - \alpha_{A'})c_s = \beta_1(c_{s-1} + c_{s+1}), & s \text{ even}, \\ & 0 \leq s \leq r \\ (E - \alpha_{B'})c_s = \beta_1(c_{s-1} + c_{s+1}), & s \text{ odd}, \end{cases} \quad (9)$$

and

$$\begin{cases} (E - \alpha_A)c_m = \beta_2(c_{m-1} + c_{m+1}), & m \text{ even}, \\ & r + 1 \leq m \leq N \\ (E - \alpha_B)c_m = \beta_2(c_{m-1} + c_{m+1}), & m \text{ odd}. \end{cases} \quad (10)$$

The perturbations introduced by the presence of the adatom at the end of the

chain and by the interaction between the last metal atom in the chain and the first atom of the support are described by some new Coulombic and resonance integrals. The adatom is characterized by a Coulomb integral $H_{\lambda\lambda} \equiv \alpha^*$, which is different from that of the atoms of the chain. The effect of the adatom on the first atom of metal of the chain is accounted for by the Coulomb integral $\alpha_{A'}^*$ (replacing $\alpha_{A'}$ for the bulk) and by the resonance integral β_1^* between the adatom and the nearest atom of metal. The resonance integral between the last metal atom and the first atom of the support is denoted by β_{12} , which is different from both β_1 and β_2 . Since the support is semi-infinite, i.e., N is large, the boundary condition for $n = N$ cannot affect the conditions near $n = r$ and $n = 0$; hence one may assume $c_N = 0$. Therefore, Eqs. (9) and (10) for the unidimensional chain model are to be solved for the boundary conditions:

$$(E - \alpha^*)c_\lambda = \beta_1^*c_0, \quad (11)$$

$$(E - \alpha_{A'}^*)c_0 = \beta_1^*c_\lambda + \beta_1c_1, \quad (12)$$

$$(E - \alpha_{B'})c_r = \beta_1c_{r-1} + \beta_{12}c_{r+1}, \quad (13)$$

$$(E - \alpha_A)c_{r+1} = \beta_{12}c_r + \beta_2c_{r+2}, \quad (14)$$

$$c_N = 0. \quad (15)$$

2. Solutions of the Equations and the Eigenvalue Equation

In order to solve the difference Eqs. (9) and (10), solutions of the form

$$c_m = x^m; \quad m \text{ even}, \quad (16a)$$

$$c_m = y^m; \quad m \text{ odd}, \quad (16b)$$

are sought. The general solutions of Eqs. (10) for the substrate (App. A), satisfying the boundary condition (15), are

$$\begin{aligned} c_m &= A_2 \sin(N - m)\theta_2; \quad m \text{ even}, \\ c_m &= K_2 A_2 \sin(N - m)\theta_2; \quad m \text{ odd}, \end{aligned} \quad (17)$$

where A_2 is a constant, and

$$K_2 = 2\beta_2 \cos \theta_2 / (E - \alpha_B). \quad (18)$$

The forms of Eq. (17) arise as a result of introducing the parameter θ_2 via

$$X^2 - z^2 = 4 \cos^2 \theta_2, \quad (19)$$

where

$$\begin{aligned} X_2 &= (E - \bar{\alpha}_2)/\beta_2, \\ z_2 &= (\alpha_A - \alpha_B)/2\beta_2, \\ \bar{\alpha}_2 &= (\alpha_A + \alpha_B)/2. \end{aligned} \quad (20)$$

The quantities X_2 and z_2 represent the dimensionless energy and composition parameter of the substrate, respectively.

Similarly (App. A), the solutions of Eqs. (9) for the metal are

$$\begin{aligned} c_s &= A_1 \cos s\theta_1 + B_1 \sin s\theta_1; \quad s \text{ even}, \\ c_s &= K_1(A_1 \cos s\theta_1 + B_1 \sin s\theta_1); \quad s \text{ odd}, \end{aligned} \quad (21)$$

where A_1 and B_1 are constants,

$$\begin{aligned} K_1 &= 2\beta_1 \cos \theta_1 / (E - \alpha_{B'}) \\ &= 2 \cos \theta_1 / (X_1 + z_1) \\ &= [(E - \alpha_{A'}) / (E - \alpha_{B'})]^{1/2}, \end{aligned} \quad (22)$$

$$X_1^2 - z_1^2 = 4 \cos^2 \theta_1, \quad (23)$$

and

$$\begin{aligned} X_1 &= (E - \bar{\alpha}_1)/\beta_1, \\ z_1 &= (\alpha_{A'} - \alpha_{B'})/2\beta_1, \\ \bar{\alpha}_1 &= (\alpha_{A'} + \alpha_{B'})/2. \end{aligned} \quad (24)$$

The quantities X_1 and z_1 are the dimensionless energy and composition parameter of the metal alloy, respectively.

Inserting Eq. (21) into Eq. (11) for c_0 , one obtains the adatom wave function coefficient

$$\begin{aligned} c_\lambda &= \eta_1' A_1 / (X_1 - z_1 + z'') \\ &= \eta_1' A_1 / (z'' + 2K_1 \cos \theta_1) \end{aligned} \quad (25)$$

where

$$\eta_1' = \beta_1^* / \beta_1, \quad z'' = (\alpha_{A'} - \alpha^*) / \beta_1. \quad (26)$$

The quantities z'' and η_1' are dimensionless parameters arising because of the adatom at the end of the chain.

The parameters θ_1 and θ_2 , introduced in Eqs. (19) and (23), are not independent quantities. Eliminating E between Eqs. (19) and (23), we can express θ_2 in terms of θ_1 by means of

$$2 \cos \theta_2 = \{[\sigma \pm \eta(z_1^2 + 4 \cos^2 \theta_1)^{1/2}]^2 - z_2^2\}^{1/2}, \quad (27)$$

where

$$\sigma = (\bar{\alpha}_1 - \bar{\alpha}_2) / \beta_2, \quad \eta = \beta_1 / \beta_2. \quad (28)$$

Introducing the solutions (17) and (21) into the boundary conditions (12), (13) and

(14), we obtain the system of homogeneous equations

$$[(z' + K_1 \cos \theta_1)(z'' + 2K_1 \cos \theta_1) - \eta_1^2]A_1 - [K_1 \sin \theta_1(z'' + 2K_1 \cos \theta_1)]B_1 = 0, \quad (29)$$

$$[K_1 \cos r\theta_1]A_1 + [K_1 \sin r\theta_1]B_1 - \left[\frac{K_2}{\eta_{21}} \sin(N - r)\theta_2 \right] A_2 = 0, \quad (30)$$

$$[\cos(r + 1)\theta_1]A_1 + [\sin(r + 1)\theta_1]B_1 - [\eta_{12} \sin(N - r - 1)\theta_2]A_2 = 0, \quad (31)$$

where

$$\begin{aligned} z' &= (\alpha_{A'} - \alpha_{A'^*})/\beta_1, \\ \eta_{12} &= \beta_{12}/\beta_1, \\ \eta_{21} &= \beta_{12}/\beta_2. \end{aligned} \quad (32)$$

The quantity z' is a dimensionless parameter characterizing the first metal atom. The quantities η_{12} and η_{21} are dimensionless parameters characterizing the interaction between the first atom of the substrate and the nearest metal atom.

The system of homogeneous Eqs. (29), (30) and (31) has nontrivial solutions, if the determinant composed of the quantities which multiply A_1 , B_1 and A_2 vanishes,

$$\begin{vmatrix} (z' + K_1 \cos \theta_1) & -K_1 \sin \theta_1(z'' + 2K_1 \cos \theta_1) & 0 \\ \times (z'' + 2K_1 \cos \theta_1) - \eta_1^2 & & \\ K_1 \cos r\theta_1 & K_1 \sin r\theta_1 & -\frac{K_2}{\eta_{21}} \sin(N - r)\theta_2 \\ \cos(r + 1)\theta_1 & \sin(r + 1)\theta_1 & -\eta_{12} \sin(N - r - 1)\theta_2 \end{vmatrix} = 0 \quad (33)$$

The determinant (33) can be rewritten in the form

$$\frac{B_1}{A_1} = \frac{\cos(r + 1)\theta_1 f(\theta_2) - H_c \cos r\theta_1}{H_c \sin r\theta_1 - f(\theta_2) \sin(r + 1)\theta_1}, \quad (36)$$

$$\frac{A_2}{A_1} = \frac{K_1 \eta_{21} \sin \theta_1}{K_2 \sin(N - r - 1)\theta_2 [f(\theta_2) \sin(r + 1)\theta_1 - H_c \sin r\theta_1]}. \quad (37)$$

$$\left\{ \begin{aligned} & z' + K_1 \cos \theta_1 \\ & - K_1 \frac{\cos(r + 1)\theta_1 f(\theta_2) - H_c \cos r\theta_1}{H_c \sin r\theta_1 - f(\theta_2) \sin(r + 1)\theta_1} \sin \theta_1 \end{aligned} \right\} \times (z'' + 2K_1 \cos \theta_1) = \eta_1^2, \quad (34)$$

where

$$\begin{aligned} f(\theta_2) &= \sin(N - r)\theta_2 / \sin(N - r - 1)\theta_2 \\ &= \cos \theta_2 + \cot(N - r - 1)\theta_2 \sin \theta_2, \end{aligned} \quad (35)$$

and

$$H_c = K_1 \eta_{21} \eta_{12} / K_2.$$

Equation (34) is the eigenvalue equation for the allowed energy levels. It involves a number of dimensionless parameters which take into account the chain of metal atoms and the perturbation effects of the two interfaces (those of the adatom and of the support) on the state of the electron. Depending upon the values of these parameters, either or both of θ_l ($l = 1, 2$), determined by Eqs. (34) and (27), can be real or complex. Real values of both θ 's represent nonlocalized volume states, since they lead to periodical wave functions which spread throughout the entire system composed of metal and support; complex values of both θ 's represent localized states, because they lead to wave functions composed of exponentials in each of the layers. The localization point has the highest probability density. Real values for one of the θ 's and complex values for the other lead to states for which the wave function is periodic in one of the layers and exponential in the other. The name composite states is given to them.

For each of the eigenvalues of Eq. (34)

the system of homogeneous Eqs. (29), (30), and (31) leads to

3. Volume States

The real values of θ_l are restricted to the range $0 \leq \theta_l \leq \pi$, for which we have $0 \leq \cos^2 \theta_l \leq 1$. It follows from Eqs. (19) and (23) that the allowed energies lie in two bands, the edges of which have upper or lower bounds given by the expressions:

$$X_l = \pm (z_l^2 + 4)^{1/2} \text{ for } \cos^2 \theta_l = 1 (l = 1, 2), \quad (38)$$

$$X_l = \pm z_l \quad \text{for } \cos^2 \theta_l = 0 (l = 1, 2). \quad (39)$$

In terms of the energy E , Eqs. (38) and (39) can be written as

$$E_{\pm O, l} = \bar{\alpha}_l \pm \beta_l (z_l^2 + 4)^{1/2}, \quad (40)$$

$$E_{\pm I, l} = \bar{\alpha}_l \pm \beta_l z_l, \quad (41)$$

where the subscripts $O(I)$ refers to the outer (inner) bounds of the energy levels. The sign $+(-)$ indicates the highest (lowest) bound.

Each of the mathematical conditions $0 < \theta_1 < \pi$ and $0 < \theta_2 < \pi$ leads to two bands (Fig. 2a). Because the energy levels E are a consequence of the interactions of the electron with the complete system (metal plus support), the allowed values of the energy for the volume states will be those which satisfy both mathematical conditions simultaneously.

Depending upon the values of the energy bounds $E_{\pm O, l}$ and $E_{\pm I, l}$, several possibilities exist. Some are represented in Fig. 2a-e. In each of these figures, the bands I are obtained from the conditions $\cos^2 \theta_1 = 1$ and $\cos^2 \theta_1 = 0$ and the bands II from the conditions $\cos^2 \theta_2 = 1$ and $\cos^2 \theta_2 = 0$; the bands III contain the regions which superpose from the previous bands. The edges of the bands III represent bounds (upper or lower) for the volume states.

As mentioned before, the wave functions for nonlocalized states are periodic. However, the amplitudes and periods of the wave function coefficients are not the same in the metal and support.

In principle, one may observe that, within the framework of the LCAO approximation, situations may arise for which no volume states exist (Fig. 2e). The absence of volume states implies the presence of composite states (but the existence of composite states does not exclude the possibilities of volume states). For instance, the wave functions can be periodic in the metal layer and decay in the support. In this case the electron belongs to the whole metal layer.

4. Localized States

Complex roots of the form

$$\theta_l = \mu_l + i\xi_l \quad (42)$$

generate the nonperiodic wave functions:

$$c_s = A_1(\cos s\mu_1 \cosh s\xi_1 - i \sin s\mu_1 \sinh s\xi_1) + B_1(\sin s\mu_1 \cosh s\xi_1 + i \cos s\mu_1 \sinh s\xi_1); \quad s \text{ even,}$$

$$c_s = K_1[A_1(\cos s\mu_1 \cosh s\xi_1 - i \sin s\mu_1 \sinh s\xi_1) + B_1(\sin s\mu_1 \cosh s\xi_1 + i \cos s\mu_1 \sinh s\xi_1)]; \quad s \text{ odd,} \quad (43a)$$

in metal, and

$$c_m = A_2[\sin(N-m)\mu_2 \cosh(N-m)\xi_2 + i \cos(N-m)\mu_2 \sinh(N-m)\xi_2]; \quad m \text{ even}$$

$$c_m = K_2 A_2[\sin(N-m)\mu_2 \cosh(N-m)\xi_2 + i \cos(N-m)\mu_2 \sinh(N-m)\xi_2]; \quad m \text{ odd,} \quad (43b)$$

in support.

Substituting Eq. (42) into Eqs. (19) and (23), the condition that the dimensionless energy should be a real quantity leads to

$$\mu_l = \frac{1}{2}k\pi; \quad k = 0, 1, 2, \dots \quad (44)$$

From this expression, two types of solutions can be generated, depending on whether k is even or odd. However, only $k = 0, 2$, and $k = 1, 3$ need be considered, because all other values repeat these solutions. Hence, from Eq. (42) we have

$$\theta_l = i\xi_l, \quad \pi + i\xi_l; \quad k \text{ even,} \quad (45a)$$

$$\theta_l = \pi/2 + i\xi_l, \quad 3\pi/2 + i\xi_l; \quad k \text{ odd.} \quad (45b)$$

As shown in Secs. 5 and 6, when k is even, the energies calculated from Eqs. (19) and (23) lie outside the main energy bands of the volume states; such states are called *outer states*; when k is odd, the energies calculated from Eqs. (19) and (23) are located inside the forbidden energy gap; such states are called *inner states*.

Information about the properties of the states described by the wave functions (43a) and (43b) are obtained from the probability density. The probability density is equal to $|c_s|^2$. For θ_2 given by Eqs. (45a) and (45b) the probability density decreases exponentially within the support. Using Eq. (21), the wave function coefficients for the metal can be rewritten as

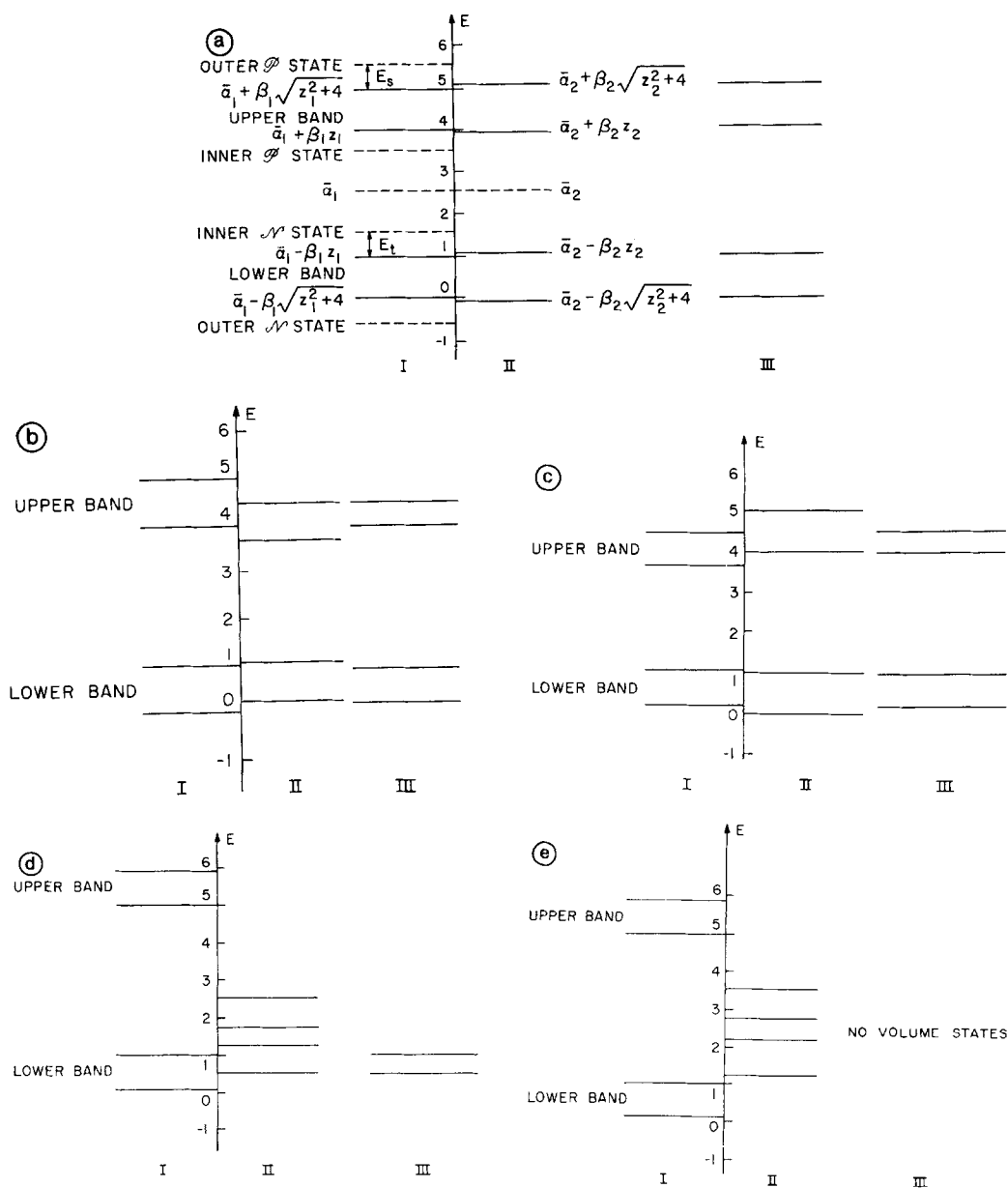


FIG. 2. Energy spectrum of supported metal for the volume states: (a) $z_1 = 1.5, z_2 = 1.35, \beta_1 = 1, \beta_2 = 1.1, \bar{\alpha}_1 = 2.5, \bar{\alpha}_2 = 2.49$; (b) $z_1 = 1.5, z_2 = 1.7, \beta_1 = 1, \beta_2 = 0.8, \bar{\alpha}_1 = 2.5, \bar{\alpha}_2 = 2.36$; (c) $z_1 = 1.7, z_2 = 1.5, \beta_1 = 0.8, \beta_2 = 1.0, \bar{\alpha}_1 = 2.36, \bar{\alpha}_2 = 2.5$; (d) $z_1 = 2.0, z_2 = 0.5, \beta_1 = 1.0, \beta_2 = 0.5, \bar{\alpha}_1 = 3.0, \bar{\alpha}_2 = 1.5$; (e) $z_1 = 2.0, z_2 = 0.5, \beta_1 = 1.0, \beta_2 = 0.5, \bar{\alpha}_1 = 3.0, \bar{\alpha}_2 = 2.45$.

$$c_s = \frac{1}{2}(1 + K_1)[(A_1 - iB_1)e^{is\theta_1} + (A_1 + iB_1)e^{-is\theta}] \quad (46) \quad \text{where} \quad c_s = (\pm 1)^s [a_1 e^{s\epsilon_1} + b_1 e^{-s\epsilon_1}] \quad (47)$$

Considering the values for θ_1 from (45a), one obtains

$$a_1 = \frac{1}{2}(1 + K_1)(A_1 + iB_1), \quad b_1 = \frac{1}{2}(1 + K_1)(A_1 - iB_1). \quad (48)$$

The plus (minus) sign in Eq. (47) corresponds to the first (second) Eq. (45a). The probability density is given by

$$|c_s|^2 = |a_1|^2 e^{2s\xi_1} + |b_1|^2 e^{-2s\xi_1} + 2\text{Re}[a_1 b_1^*], \quad (49)$$

where b_1^* is the complex conjugate of b_1 .

If $|a_1|^2 < |b_1|^2 e^{-4r\xi_1}$, then $d|c_s|^2/ds$ is negative, and the electron is "localized" at the adatom-metal surface. If $|a_1|^2 > |b_1|^2$, then $d|c_s|^2/ds$ is positive, and the electron is localized at the metal-support interface. If $|b_1|^2 e^{-4r\xi_1} < |a_1|^2 < |b_1|^2$, $d|c_s|^2/ds$ changes sign inside the metal layer, and the probability density is high both at the adatom-metal surface and metal-support interface. Considering the values for θ_1 from Eq. (45b), similar results are obtained if one replaces a_1 and b_1 by

$$a_2 = \frac{1}{2}(1 + K_1)(-B_1 - iA_1) \quad \text{and} \\ b_2 = \frac{1}{2}(1 + K_1)(B_1 - iA_1). \quad (50)$$

Values of ξ_1 are obtained introducing Eqs. (45a) or (45b) into the eigenvalue Eq. (34) (see Sects. 5 and 6).

The complex roots (42) lead to states which are localized either at the surface of metal and adatom or at the metal-support interface. Under some conditions (specified above) the probability density is high both at the surface of metal and adatom and at the metal-support interface. Of course, the probability density in the latter case may be higher (or even much higher) at one of these points.

5. Outer Localized States

The existence conditions of the outer localized states are found by substituting θ_1 from Eq. (45a) into the eigenvalue Eq. (34) [Eq. (27) is used to eliminate θ_2 from Eq. (34)]. For large values of N , $f(\theta_2)$ can be approximated by g , where (see App. B)

$$g = \frac{1}{2}\{[\sigma \pm \eta(z_1^2 + 4 \cosh^2 \xi_1)^{1/2}]^2 - z_2^2\}^{1/2} \\ + \left(\frac{1}{4}\{[\sigma \pm \eta(z_1^2 + 4 \cosh^2 \xi_1)^{1/2}]^2 - z_2^2\} - 1\right)^{1/2}. \quad (51)$$

One obtains

$$[z' \pm K_{\pm 1} \cosh \xi_1 \\ \mp K_{\pm 1} \frac{g \cosh(r+1)\xi_1 - H_c \cosh r\xi_1}{H_c \sinh r\xi_1 - g \sinh(r+1)\xi_1} \sinh \xi_1] \\ \times [z'' \pm 2K_{\pm 1} \cosh \xi_1] = \eta_1^2, \quad (52)$$

where

$$K_{\pm 1} = [(z_1^2 + 4 \cosh^2 \xi_1)^{1/2} \mp z_1]/2 \cosh \xi_1. \quad (53)$$

When solutions of Eq. (52) exist, they lead to energies above the top edge of the upper band and below the bottom edge of the lower band. Indeed, the upper signs in Eqs. (51), (52) and (53) correspond to solution of Eq. (34) with $\theta_1 = i\xi_1$ and, hence, energy

$$E = \bar{\alpha}_1 + \beta_1(z_1^2 + 4 \cosh^2 \xi_1)^{1/2}.$$

If β_1 is positive, such states are situated above the top edge of the upper band (anti-bonding) (see Fig. 2). The lower sign corresponds to solution of Eq. (34) with $\theta_1 = \pi + i\xi_1$ and, hence, energy

$$E = \bar{\alpha}_1 - \beta_1(z_1^2 + 4 \cosh^2 \xi_1)^{1/2}.$$

If β_1 is positive, these states are situated below the bottom edge of the lower band (bonding state). The state will be called \wp state when $X_1 > 0$ and \mathfrak{X} state when $X_1 < 0$. In Fig. 2a, the depth of the outer level below (above) the bottom (top) of the lower (upper) band is

$$E_s = |\beta_1(z_1^2 + 4 \cosh^2 \xi_1)^{1/2} \\ - |\beta_1(z_1^2 + 4)^{1/2}|. \quad (54)$$

For large band gap width Eq. (54) can be approximated by

$$E_s \approx \frac{2\beta_1 \sinh^2 \xi_1}{z_1}. \quad (55)$$

For the situation depicted in the Fig. 2a, the energy levels of the outer localized states coincide for $\xi_1 = 0$ with the top of the upper band or the bottom of the lower band of the volume states. Taking $\xi_1 = 0$ in Eq. (52), one obtains

$$\left[z' \pm 2K_{\pm 1} \mp K_{\pm 1} \frac{(r-1)H_c - rP_{\pm}}{rH_c - (r+1)P_{\pm}} \right] \\ \times [z'' \pm 2K_{\pm 1}] = \eta_1^2, \quad (56)$$

where

$$K_{\pm 1} = [(z_1^2 + 4)^{1/2} \mp z_1]/2, \\ P_{\pm} = \frac{1}{2}(y_{\pm})^{1/2} + \left[\frac{1}{4}(y_{\pm}) - 1\right]^{1/2}, \\ y_{\pm} = [\sigma \pm \eta(z_1^2 + 4)^{1/2}]^2 - z_2^2. \quad (57)$$

Because of the plus and minus signs, Eq. (56) represents two different equations. Because one localized state changes to a

nonlocalized state for $\xi_1 = 0$, each of these equations is the boundary between regions containing two and one, or one and zero localized outer states. A representation in the $z'z''$ -plane of Eq. (56) is given in Fig. 3a-c for $\eta_1'^2 = 1$ and for various values of the parameters. The various regions are labeled according to the sign of X and the number and nature of the localized outer states occurring. Thus, six regions of localized states exist. For instance, in a \mathfrak{N}^2 region two outer \mathfrak{N} states occur, while in a $\mathcal{O}\mathfrak{N}$ region there are one outer \mathcal{O} state and one outer \mathfrak{N} state, and so on. The shaded area in Fig. 3 represents values of z' and z'' for which no outer localized states occur. Consequently, depending on the interaction parameters z', z'' and η_1' between the adatom

and the supported metal catalyst, the system may have two, one or no localized outer states. In the region in which

$$\eta_1'^2 < 2(z_1'^2 + 2) - K_{+1}^2 \left[\frac{(r-1)H_c - rP_+}{rH_c - (r+1)P_+} \right] - K_{-1}^2 \left[\frac{(r-1)H_c - rP_-}{rH_c - (r+1)P_-} \right], \quad (58)$$

no outer localized state exists. The area of the closed region, is given by

$$v = 2(z_1'^2 + 2) - K_{+1}^2 \left[\frac{(r-1)H_c - rP_+}{rH_c - (r+1)P_+} \right] - K_{-1}^2 \left[\frac{(r-1)H_c - rP_-}{rH_c - (r+1)P_-} \right]. \quad (59)$$

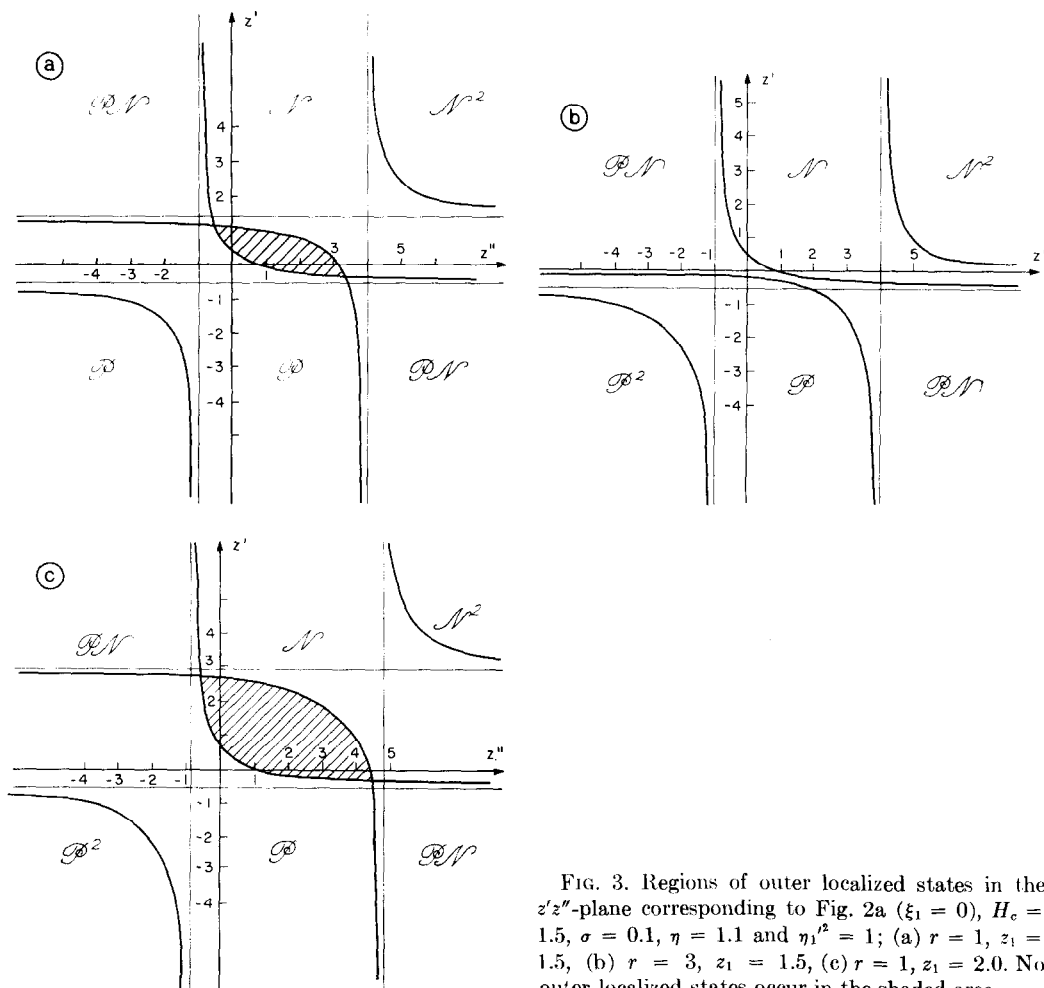


FIG. 3. Regions of outer localized states in the $z'z''$ -plane corresponding to Fig. 2a ($\xi_1 = 0$), $H_c = 1.5$, $\sigma = 0.1$, $\eta = 1.1$ and $\eta_1'^2 = 1$; (a) $r = 1$, $z_1 = 1.5$, (b) $r = 3$, $z_1 = 1.5$, (c) $r = 1$, $z_1 = 2.0$. No outer localized states occur in the shaded area.

In Fig. 4 v is plotted vs r for $z_1 = 1.5$ and various values of the parameters H_c and η . As expected, if the number of the metal atoms increases, the influence of the support on the whole system decreases. In the range of values used in Fig. 4 for the various parameters, the effect of the support can be neglected if the number of metal atoms $r + 1$ is between 5 and 10.

6. Inner Localized States

The occurrence of the inner localized states is examined by substituting Eq. (45b) into the eigenvalue Eq. (34). Eliminating θ_2 by means of Eq. (27) and approximating (because N is large) the function $f(\theta_2)$ by g_1 [Eq. (61)] (see App. B), one obtains

$$\left[z' \pm iK_{\pm 1}^{(r)} \sinh \xi_1 \mp K_{\pm 1}^{(r)} \frac{g_1 \cos(r+1)(\frac{3\pi}{2} + i\xi_1) - H_c \cos r(\frac{3\pi}{2} + i\xi_1)}{H_c \sin r(\frac{3\pi}{2} + i\xi_1) - g_1 \sin(r+1)(\frac{3\pi}{2} + i\xi_1)} \cosh \xi_1 \right] \times [z'' \pm 2iK_{\pm 1}^{(r)} \sinh \xi_1] = \eta_1^r, \quad (60)$$

where

$$g_1 = \frac{1}{2}\{h\}^{1/2} + [\frac{1}{4}(h) - 1]^{1/2},$$

$$h = [\sigma + \eta(z_1^2 - 4 \sinh^2 \xi_1)^{1/2}]^2 - z_2^2 \quad (61)$$

and

$$K_{\pm 1}^{(r)} = \pm 2i\beta_1 \sinh \xi_1 / (E - \alpha_B). \quad (62)$$

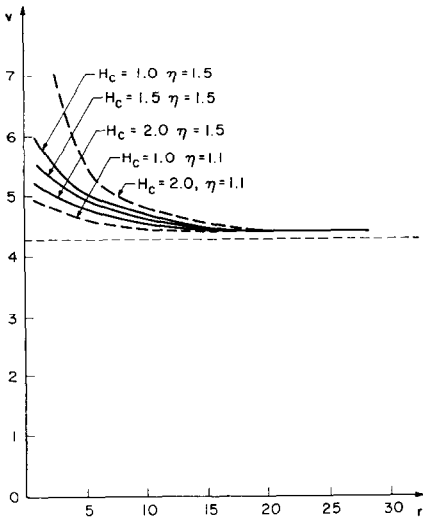


FIG. 4. Area of the region from Fig. 3 in which no outer localized states occur vs number of metal atoms.

The energies of the inner states are given by the equations

$$E = \bar{\alpha}_1 + \beta_1(z_1^2 - 4 \sinh^2 \xi_1)^{1/2}$$

and

$$E = \bar{\alpha}_1 - \beta_1(z_1^2 - 4 \sinh^2 \xi_1)^{1/2}.$$

If $\beta_1 > 0$, the first is an inner \mathcal{O} state and the second an inner \mathcal{X} state. Referring to Fig. 2a, the height of the inner level above the top of the lower band edge is

$$E_t = |\beta_1 z_1^2 - \beta_1(z_1^2 - 4 \sinh^2 \xi_1)^{1/2}|. \quad (63)$$

For large band gap width, Eq. (63) can be approximated by

$$E_t \approx 2\beta_1 (\sinh^2 \xi_1) / z_1. \quad (64)$$

In order to identify various regions of inner states, one must take into account that, for the situation represented in Fig. 2a, a localized state is transformed into a volume state when $\xi_1 = 0$. The boundaries separating the regions can thus be obtained taking $\xi_1 = 0$ in Eq. (60):

$$[z' \pm a]z'' = \eta_1 \quad (65)$$

where

$$a = \frac{-G_{\pm}}{H_1 - (r+1)P_{\pm r}}; \quad r \text{ odd}, \quad (66)$$

with

$$P_{\pm r} = \frac{1}{2}(y_{\pm r})^{1/2} + [\frac{1}{4}(y_{\pm r}) - 1]^{1/2},$$

$$y_{\pm r} = [(\sigma \pm \eta z_1)^2 - z_2^2],$$

$$G_{\pm} = P_{\pm r} / z_1, \quad H_1 = \frac{\eta_{12}\eta_{21}}{z_1 K_2}. \quad (67)$$

In fact, Eq. (65) represents two equations. Each of them separates regions having two or one inner state. They are plotted in Fig. 5 for $\eta_1^2 = 1$ and for various values of the parameters. One may observe from Fig. 5 that at least one inner state exists.

An overall picture of the nature of the localized states for the situation depicted in Fig. 2a is obtained superposing Figs. 3 and

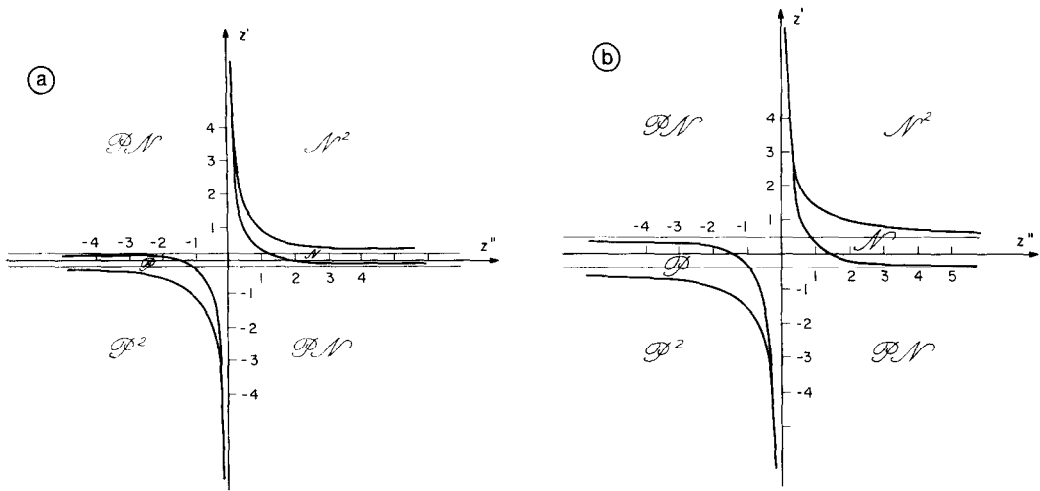


FIG. 5. Regions of inner localized states in the $z'z''$ -plane corresponding to Fig. 2a ($\xi_1 = 0$), $H_1 = 6.0$, $\sigma = 0.01$, $\eta = 0.91$, $z_1 = 1.5$, $z_2 = 1.35$, and $\eta_1'' = 1$; (a) $r = 1$, (b) $r = 3$.

5. From this superposition (Fig. 6) one may conclude that the maximum number of localized states is four. There are regions, however, in which the number of localized states is three, two or one. If it is one, then it is an inner state.

7. Nature of Localized States for the Situations Depicted in Figs. 2b and 2c

For the situation represented in Fig. 2b the transition from an outer localized state to a volume state takes place for $\xi_2 = 0$, and

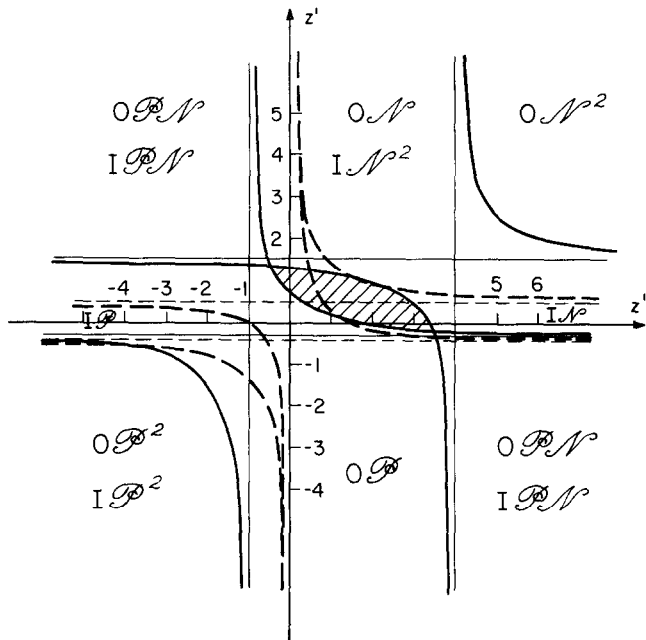


FIG. 6. Regions of outer and inner localized states corresponding to Fig. 2a (obtained by superposition of Figs. 3 and 5), $\sigma = 0.01$, $\eta = 0.91$, $z_1 = 1.5$, $z_2 = 1.35$, $\eta_1'' = 1$ and $r = 3$. (—) Separates the regions of outer localized states (O); (---) separates the regions of inner localized states (I).

the transition from an inner localized state to a volume state for $\xi_1 = 0$. In Fig. 7, we represent the corresponding outer localized states. For the situation represented in Fig. 2c, the transition from an outer localized state to a volume state takes place for $\xi_1 = 0$, and from an inner localized state to a volume state for $\xi_2 = 0$. In Fig. 8 we represent the corresponding inner states.

8. Single Component Metal on an AB Support

A figure similar to Fig. 2 can be constructed for the volume states (Fig. 9). Before the metal and support are in contact, the energy spectrum for the volume states consists of one band for the metal and two bands for the support. After contact, the whole system may have two, one or no allowed energy bands for the volume states.

Because in this case $K_1 = 1$, $z_1 = 0$ and $\alpha_{A'} = \alpha_1$, Eqs. (56), which give the boundaries between various regions of localized states, become

$$\left[z_1' \pm 2 \mp \frac{(r-1)H_s - rP_{\pm s}}{rH_s - (r+1)P_{\pm s}} \right] [z_1'' \pm 2] = \eta_1'^2, \quad (68)$$

where

$$\begin{aligned} z_1' &= (\alpha_1 - \alpha_1')/\beta_1, & z_1'' &= (\alpha_1 - \alpha_1'')/\beta_1, \\ H_s &= \eta_{12}\eta_{21}/K_2, & P_{\pm s} &= \frac{1}{2}(y_{\pm}')^{1/2} \\ & & &+ [\frac{1}{4}(y_{\pm}') - 1]^{1/2}, \quad (69) \\ y_{\pm}' &= [\sigma_s \pm 2\eta]^2 - z_2^2, & \sigma_s &= (\alpha_1 - \bar{\alpha}_2)/\beta_2. \end{aligned}$$

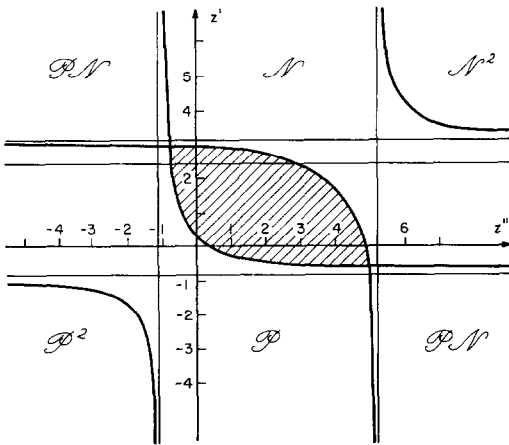


FIG. 7. Regions of outer localized states in the $z'z''$ -plane corresponding to Fig. 2b ($\xi_2 = 0$), $z_1 = 2.0$, $z_2 = 1.5$, $\sigma_1 = 0.5$, $\eta_1 = 1.1$, $H_c = 1.5$, and $\eta_1'^2 = 1$ with $r = 1$.

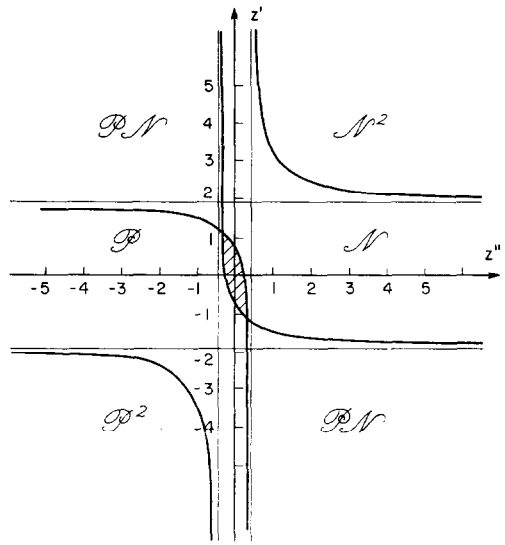


FIG. 8. Regions of inner localized states in the $z'z''$ -plane corresponding to Fig. 2c ($\xi_2 = 0$), $z_1 = 1.5$, $\eta_1 = 0.8$, $\sigma_1 = 0.3$, $z_2 = 1.7$ and $\eta_1'^2 = 1$. No inner localized states occur in the shaded area.

A representation in the $z_1'z_1''$ -plane of Eq. (68) is given in Fig. 10 for $\eta_1'^2 = 1$ and for various values of the parameters. The regions are labeled as in the previous sections.

9. Single Component Metal Supported on Single Component Metal

If a linear chain composed of a finite number of atoms of a pure metal is supported on a semi-infinite metal, $K_1 = 1$, $K_2 = 1$, $z_1 = 0$, $z_2 = 0$ and Eq. (68) becomes

$$\left[z_1' \pm 2 \mp \frac{(r-1)H_2 - rP_{\pm 2}}{rH_2 - (r+1)P_{\pm 2}} \right] [z_1'' \pm 2] = \eta_1'^2, \quad (70)$$

where

$$\begin{aligned} H_2 &= \eta_{12}\eta_{21}, \\ P_{\pm 2} &= \frac{1}{2}(\sigma_2 \pm 2\eta) + [\frac{1}{4}(\sigma_2 \pm 2\eta)^2 - 1]^{1/2}, \\ \sigma_2 &= (\alpha_1 - \alpha_2)/\beta_2. \quad (71) \end{aligned}$$

Before contact, the energy spectrum for the volume states consists of one band for the metal and one band for the support. After contact, the whole system may have one or no allowed energy bands for the volume states.

10. Nature of Surface Bonds

The values of the interaction parameters determine the nature of the bond between

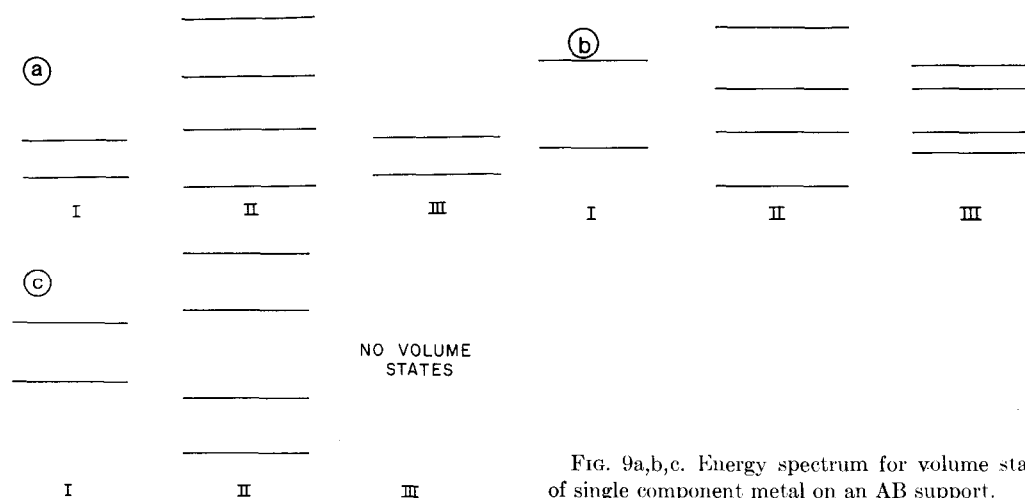


FIG. 9a,b,c. Energy spectrum for volume states of single component metal on an AB support.

the adatom and the surface of the metal for a localized state. For a localized state the electron is localized either near to the adatom and/or near to the metal-support interface. Depending on the "localization" site the bond can be classified as homopolar, anionic or cationic. The ratio R between the probability of localization of the electron on the adatom and the probability of its localization in all the other positions in the system gives information about the nature of the bond. This ratio R is given by the equation

$$R = |c_\lambda|^2 / [|c_\lambda|^2 + \sum_{n=0}^N |c_n|^2]. \quad (72)$$

Depending on the values of c_λ and all c_n , R can vary between 0 and 1. There are two extreme cases

(a) $c_\lambda = 0, \sum_{n=0}^N |c_n|^2 \neq 0$ so that $R =$

0. The electron is not localized at the adatom, and the adatom is in the cationic state.

(b) $c_\lambda \neq 0, \sum_{n=0}^N |c_n|^2 = 0$ gives $R = 1,$

and the electron is concentrated entirely on the adatom, and the adatom is in the anionic state.

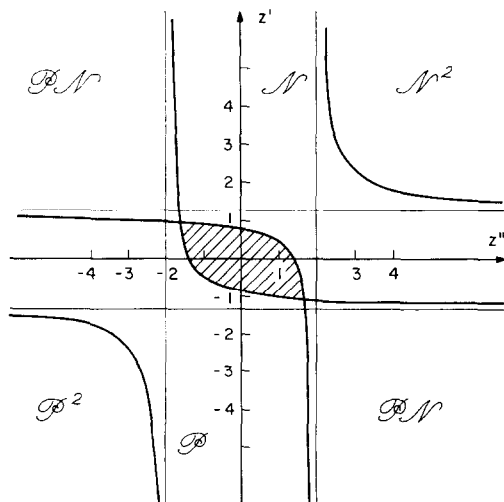


FIG. 10. Regions of localized states in the $z_1'z_1''$ -plane in the case of single component metal on an AB-type support $H_s = 1.5, \sigma_s = 0.1, \eta = 1.5, z_2 = 0.5, r = 1$ and $\eta_1'^2 = 1$.

For the homopolar bond, which is the intermediate of the two extreme cases,

$|c_\lambda|^2 = \sum_{n=0}^N |c_n|^2$ and $R = 1/2$. In this case,

the electron belongs with equal probability to both the adatom and the metal-support system. Taking the homopolar state as a reference state, we shall consider that if $R < 1/2$, the adatom is in the cationic state, and if $R > 1/2$, the adatom is in the anionic state.

The discussion which follows is based on the situation depicted in Fig. 2a.

The adatom wave function coefficient c_λ

for the outer localized states can be written as

$$c_\lambda = \eta_1' A_1 / (z'' \pm 2K_1 \cosh \xi_1). \quad (73)$$

For a \mathcal{O} state the plus sign is valid and for an \mathcal{X} state the minus sign. Then, for a homopolar outer \mathcal{O} state, we have

$$\begin{aligned} (z'' + 2K_1 \cosh \xi_1)^2 &= \frac{\eta_1'^2 A_1^2}{|c_0|^2 + \sum_{n=1}^N |c_n|^2} = \frac{\eta_1'^2}{1 + \frac{1}{A_1^2} \sum_{n=1}^N |c_n|^2} \\ &= \frac{1 + \sum_{s \text{ even}} |\cosh s\xi_1 + i \frac{B_1}{A_1} \sinh s\xi_1|^2 + K_1^2 \sum_{s \text{ odd}} |\cosh s\xi_1 + i \frac{B_1}{A_1} \sinh s\xi_1|^2}{\sum_{m \text{ even}} \frac{A_2^2}{A_1^2} \sin^2(N-m)(i\xi_2) + K_2^2 \sum_{m \text{ odd}} \frac{A_2^2}{A_1^2} \sin^2(N-m)(i\xi_2)} \quad (74) \end{aligned}$$

From Eq. (74) and the eigenvalue Eq. (52), one can obtain values of z' and z'' for which homopolar outer \mathcal{O} states occur (Fig. 11). There are two curves, both having $z' = z''$ and $z'' = -2K_1$ as asymptotes. For instance, a homopolar \mathcal{O} state is obtained for $\eta_1' = 1$, $z' = 2.00$, and $z'' = -0.68$ when $\xi_1 = 0.1$. The corresponding wave function coefficients (unnormalized) are $c_\lambda = 2.519$, $c_0 = 1.00$ and $\sum_{n=1}^N |c_n|^2 = 5.33$.

Obviously, the occurrence of a homopolar state is a special case; most values of the interaction parameters lead to states having—to a greater or lesser extent—an ionic character. The regions of occurrence of anionic or cationic localized states are represented in Fig. 12. $OA\mathcal{O}C\mathcal{O}$ means that there is an anionic \mathcal{O} outer state and a cationic \mathcal{O} outer state, $OA\mathcal{O}C\mathcal{X}$ that there is an anionic \mathcal{O} outer state and a cationic \mathcal{X} outer state, and so on. For instance, when $z' = -3$, $z'' = 0$ and $\eta_1' = 1$, one obtains $\xi_1 = 1.53$ and $X = 5.06$. The corresponding wave function coefficients are $c_\lambda = 0.18$, $c_0 = 1.0$. In this case, $R < 0.04$, and a cationic \mathcal{O} outer state occurs. However, for $z' = 0$, $z'' = -3$, and $\eta_1' = 1$, one obtains $\xi_1 = 1.50$ and $X = 4.83$, and the corresponding wave function coefficients are $c_\lambda = 8.77$, $c_0 = 1.0$,

so that $R \approx 0.95$. In this case, an anionic \mathcal{O} outer state occurs (see Fig. 12).

For a volume state, the electron may belong to any atom in the chain with probabilities depending on the nature of the atoms. This kind of bond is “metallic.”

In Table 1 several results of our com-

putations are presented. They show the effect of the number of metal atoms and the parameters z' and z'' on the nature of the bond. The values of the parameters not

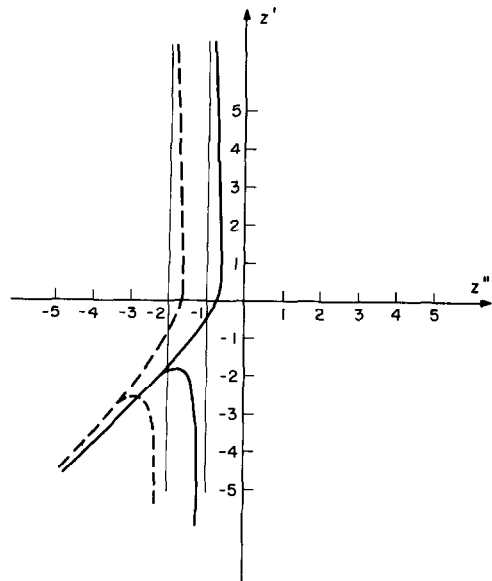


Fig. 11. Curve of homopolar \mathcal{O} outer states in the $z'z''$ -plane $z_1 = 1.5$, $H_{1c} = 1.5$, $\sigma = 0.1$, $\eta = 1.1$, $r = 1$, and $\eta_1'^2 = 1$. (—) Supported metal catalyst; (---) pure semi-infinite metal).

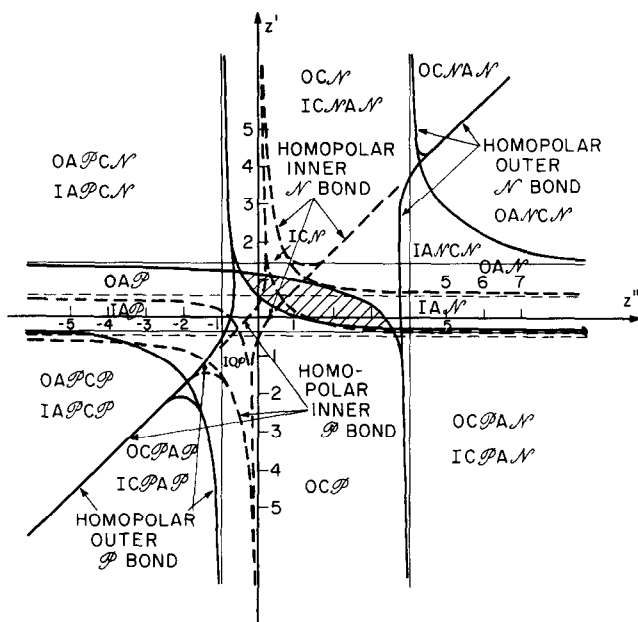


FIG. 12. Regions where homopolar, anionic, or cationic localized states may occur $H_c = 1.5, z_1 = 1.5, \sigma = 0.1, r = 1, \eta = 1.1$ and $\eta_1^z = 1$. (—) Separates the regions of outer localized states; (---) separates the regions of inner localized states.

mentioned in Table 1 are the same as in Fig. 12.

11. Composite States

For the bilayers new type of states can occur in which the wave function is periodic

in one of the layers and nonperiodic in the other. This kind of wave function will be called a composite wave function and the corresponding states composite states. Specific to these states is the fact that either θ_1 or θ_2 is imaginary. The wave function can

TABLE 1
NATURE OF LOCALIZED BONDS IN CHEMISORPTION ON SUPPORTED METALS

No. of metal atoms	z'	z''	ξ_1	X	c_A	c_0	R	Type of bond
2	-3.00	-3.20	1.66	5.64	1.01	1.00	0.5	Homopolar Φ
2	2.00	-0.68	0.1	2.508	2.519	1.00	0.5	Homopolar Φ
∞	2.00	-0.68	0.83	-1.365	-0.293	1.00	0.06	Cationic \mathfrak{K}
2	0.00	-3.00	1.50	4.83	8.77	1.00	0.95	Anionic Φ
∞	0.00	-3.00	1.10	1.66	3.125	1.00	0.89	Anionic Φ
2	-3.00	0.00	1.53	5.06	0.18	1.00	0.04	Cationic Φ
∞	-3.00	0.00	1.185	1.785	0.278	1.00	0.066	Cationic Φ
4	-3.00	0.00	1.52	5.03	0.29	1.00	0.08	Cationic Φ
12	-3.00	0.00	1.52	5.03	0.29	1.00	0.08	Cationic Φ
2	-2.00	0.00	1.23	3.98	0.40	1.00	0.12	Cationic Φ
∞	-2.00	0.00	0.86	1.393	0.358	1.00	0.1	Cationic Φ
4	-2.00	0.00	1.26	4.09	0.38	1.00	0.11	Cationic Φ
2	1.55	3.00	0.2	-2.53	-0.96	1.00	0.45	Cationic \mathfrak{K}
∞	1.55	3.00	1.19	-1.80	-1.67	1.00	0.68	Anionic \mathfrak{K}
2	0.5	0.5		2.00				Metallic

be nonperiodic in the metal and periodic in the support, and then a localized state at the metal surface and adatom can occur. The wave function can be periodic in the metal layer and exponentially decaying in the support, and in this case the electron belongs to the whole metal layer.

CONCLUSION

The support affects the chemisorption process: (a) by modifying the energies of nonlocalized volume states and those of the localized states and (b) by generating composite states, which have a periodic wave function in one of the layers and a nonperiodic wave function in the other.

The influence on the volume states is shown in Figs. 2 and 9, from which the following observations can be made. A single component finite chain of metal without support has a single band; with an AB-type support the complete system can have two bands. An A'B' finite chain of metal without support has two bands; with support there are conditions in which the whole system has only one band. Two semiconductor layers (each of them represented independently by two bands) can have a single band for the volume states (as the metals). Metal-semiconductor layers, which independently can be represented by one-two bands, may together have no volume states.

The influence of the support on the localized states is shown in Table 1. Depending on the number of atoms of the metal and the nature of the support, the localized bond can change from anionic to cationic.

For the range of parameters used in this paper, the number of metal atoms has an effect on chemisorption if it is less than 5 to 10.

States specific to bilayers occur. They have periodic wave functions in one of the layers and nonperiodic wave functions in the other. If the wave function coefficients are larger in the layer having a periodic wave function, the electron will belong to that whole layer.

ACKNOWLEDGMENT

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APPENDIX A

Solutions of Eqs. (9) and (10)

Inserting Eq. (16a) in Eq. (10a), and Eq. (16b) in Eq. (10b) yields

$$(E - \alpha_A)x^m = \beta_2(y^{m-1} + y^{m+1}); \quad m \text{ even}, \quad (\text{A1})$$

$$(E - \alpha_B)y^m = \beta_2(x^{m-1} + x^{m+1}); \quad m \text{ odd}. \quad (\text{A2})$$

i. For m Even

Eliminating y between Eqs. (A1) and (A2) one obtains

$$(E - \alpha_A)(E - \alpha_B)x^m = \beta_2^2(x^{m+2} + 2x^m + x^{m-2}),$$

$$\text{i.e., } (E - \alpha_A)(E - \alpha_B)x^2 = \beta_2^2(x^4 + 2x^2 + 1) = \beta_2^2(x^2 + 1)^2,$$

$$\text{or } \pm[(E - \alpha_A)(E - \alpha_B)]^{1/2}x = \beta_2(x^2 + 1),$$

which can be written as

$$x^2 - \Delta x + 1 = 0, \quad (\text{A3})$$

where

$$\Delta = \pm[(E - \alpha_A)(E - \alpha_B)]^{1/2}/\beta_2. \quad (\text{A4})$$

The solution of Eq. (A3) is

$$x = \Delta/2 \pm [(\Delta/2)^2 - 1]^{1/2}. \quad (\text{A5})$$

Denoting

$$\Delta = 2 \cos \theta_2, \quad (\text{A6})$$

x can be written as

$$x = \cos \theta_2 \pm i \sin \theta_2 = \exp(\pm i\theta_2). \quad (\text{A7})$$

Thus, the general solution of (A1) may be expressed as

$$x^m = c_m = C e^{im\theta_2} + D e^{-im\theta_2} = A_3 \cos m\theta_2 + B_3 \sin m\theta_2 \quad (\text{A8})$$

in which

$$A_3 = C + D, \quad B_3 = i(C - D). \quad (\text{A9})$$

Because $c_N = 0$, Eq. (A8) leads to

$$B_3 = -\frac{A_3 \cos N\theta_2}{\sin N\theta_2}.$$

Therefore

$$\begin{aligned} c_m &= A_3 \cos m\theta_2 - \frac{A_3 \cos N\theta_2}{\sin N\theta_2} \sin m\theta_2 \\ &= \frac{A_3}{\sin N\theta_2} \sin(N - m)\theta_2 \\ &= A_2 \sin(N - m)\theta_2. \end{aligned} \quad (\text{A10})$$

ii. For m Odd

Introducing x^m from (A10) in Eq. (A2), one obtains

$$(E - \alpha_B)y^m = \beta_2(A_2 \sin(N - m + 1)\theta_2 + A_2 \sin(N - m - 1)\theta_2). \quad (A11)$$

Because [Eq. (16b)] $y^m = c_m$, Eq. (A11) becomes

$$y^m = c_m = K_2 A_2 \sin(N - m)\theta_2, \quad (A12)$$

where

$$K_2 = 2\beta_2 \cos \theta_2 / (E - \alpha_B). \quad (A13)$$

From Eqs. (A4) and (A6), one obtains

$$4\beta_2^2 \cos^2 \theta_2 = (E - \alpha_A)(E - \alpha_B). \quad (A14)$$

Defining a dimensionless energy by

$$X_2 = (E - \bar{\alpha}_2) / \beta_2, \quad \bar{\alpha}_2 = (\alpha_A + \alpha_B) / 2, \quad (A15)$$

Eq. (A14) can be written as

$$X_2^2 - z_2^2 = 4 \cos^2 \theta_2, \quad (A16)$$

where

$$z_2 = (\alpha_A - \alpha_B) / 2\beta_2 \quad (A17)$$

$$\begin{aligned} f &= \lim_{N \rightarrow \infty} f(\theta_2) \\ &= \frac{e^{(N-r)\xi_2} [\sin(N-r)\mu_2 + i \cos(N-r)\mu_2]}{e^{(N-r-1)\xi_2} [\sin(N-r-1)\mu_2 + i \cos(N-r-1)\mu_2]} \\ &= \frac{e^{\xi_2} [\sin(N-r)\mu_2 + i \cos(N-r)\mu_2] (-i)}{[\sin(N-r-1)\mu_2 + i \cos(N-r-1)\mu_2] (-i)} \\ &= \frac{e^{\xi_2} e^{-i(N-r)\mu_2} / e^{-i(N-r-1)\mu_2}}{e^{i\xi_2}} \\ &= e^{(i\xi_2 - i\mu_2)}. \end{aligned} \quad (B2)$$

is the composition parameter of the substrate.

Similarly, the solutions of Eqs. (9) for the metal, by inserting Eq. (16a) in Eq. (9a), and Eq. (16b) in Eq. (9b), are

$$\begin{aligned} c_s &= A_1 \cos s\theta_1 + B_1 \sin s\theta_1, & s \text{ even,} \\ c_s &= K_1(A_1 \cos s\theta_1 + B_1 \sin s\theta_1), & s \text{ odd,} \end{aligned} \quad (A18)$$

where

$$\begin{aligned} K_1 &= 2\beta_1 \cos \theta_1 / (E - \alpha_{B'}) \\ &= 2 \cos \theta_1 / (X_1 + z_1) \\ &= [(E - \alpha_{A'}) / (E - \alpha_{B'})]^{1/2}. \end{aligned} \quad (A19)$$

The forms of (A18) arise by introducing the parameter θ_1 via

$$X_1^2 - z_1^2 = 4 \cos^2 \theta_1, \quad (A20)$$

where

$$\begin{aligned} X_1 &= (E - \bar{\alpha}_1) / \beta_1, \\ z_1 &= (\alpha_{A'} - \alpha_{B'}) / 2\beta_1, \\ \bar{\alpha}_1 &= (\alpha_{A'} + \alpha_{B'}) / 2. \end{aligned} \quad (A21)$$

X_1 and z_1 are the dimensionless energy and composition parameter of the metal, respectively.

APPENDIX B

Derivations of Eqs. (46) and (56)

Inserting Eq. (42) in Eq. (35) yields

For large value of N , Eq. (B1) can be approximated by

Since $\theta_2 = \mu_2 + i \xi_2$, Eq. (B2) can be written

$$\text{as} \quad f = e^{-i\theta_2} = \cos \theta_2 - i \sin \theta_2. \quad (B3)$$

From Eqs. (27) and (B3), one obtains

$$f = \frac{1}{2}\{\sigma \pm \eta(z_1^2 + 4 \cos^2 \theta_1)^{1/2}\}^2 - z_2^2\}^{1/2} + \left(\frac{1}{4}\{\sigma \pm \eta(z_1^2 + 4 \cos^2 \theta_1)^{1/2}\}^2 - z_2^2\} - 1\right)^{1/2}. \quad (\text{B4})$$

For $\theta_1 = i\xi_1$, $\pi + i\xi_1$, Eq. (B4) becomes

$$g = \frac{1}{2}\{\sigma \pm \eta(z_1^2 + 4 \cosh^2 \xi_1)^{1/2}\}^2 - z_2^2\}^{1/2} + \left(\frac{1}{4}\{\sigma \pm \eta(z_1^2 + 4 \cosh^2 \xi_1)^{1/2}\}^2 - z_2^2\} - 1\right)^{1/2}. \quad (\text{B5})$$

For $\theta_1 = (\pi/2) + i\xi_1$, $(3\pi/2) + i\xi_1$, Eq. (B4) becomes

$$g_1 = \frac{1}{2}\{\sigma \pm \eta(z_1^2 - 4 \sinh^2 \xi_1)^{1/2}\}^2 - z_2^2\}^{1/2} + \left(\frac{1}{4}\{\sigma \pm \eta(z_1^2 - 4 \sinh^2 \xi_1)^{1/2}\}^2 - z_2^2\} - 1\right)^{1/2}. \quad (\text{B6})$$

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