© *Proc. Indian natn. Sci. Acad.*, 51, A, No. 1, 1985, pp. 98-123.
Printed in India.

THEORETICAL ASPECTS OF CHEMISORPTION BY METALS*+

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1. INTRODUCTION

THE clean surfaces of many solids are very reactive. Even in a good vacuum (10^{-6} torr+), most metals will become covered with a layer of *adsorbed* gas (oxygen or nitrogen) in less than a minute, and this is because nearly every gas molecule which hits the metal surface, sticks to it. In other words, the sticking coefficient is nearly unity.

Molecules may be *physisorbed* or *chemisorbed*. The former is shorthand for physically adsorbed, the latter for chemically adsorbed. Rare gases (He, Ne,... Xe) are physisorbed by metals. No chemical bond is formed, but the atom is attracted to the surface by the Van der Waals force varying with distance from the surface like $(\text{distance})^{-4}$. At short distances when the electron clouds of the gas atom and the metal begin to overlap, a strong repulsive force develops. This repulsion is due essentially to the operation of the Pauli Exclusion Principle; the metal electrons must avoid the electrons in the doubly occupied orbitals of the rare gas atom, and this raises their kinetic energy. The addition of the long-range attractive, and the short-range repulsive forces leads to a potential energy curve with a shallow minimum of depth about 1 kJ mol^{-1}, (Fig. 1).

In *chemisorption*, a chemical bond is formed between the solid (the substrate), and the adsorbed species (the adsorbate). We call this bond the surface bond, or

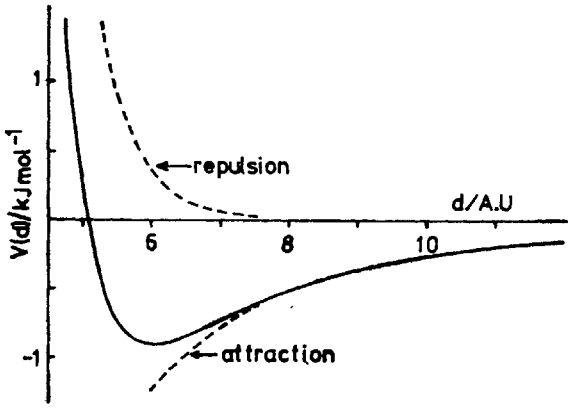


FIG. 1. The potential energy curve for a rare gas atom near a metal showing the attractive, and repulsive contributions.

* Paper presented at the Symposium on Physics and Chemistry of Surfaces held at INSA, New Delhi from September 28-30, 1984.

+ 760 torr ≡ 1 atmosphere pressure

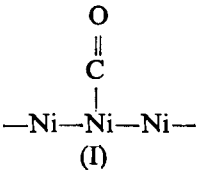
the chemisorption bond. Existing chemical bonds in the gas molecule may be strongly perturbed when the surface bond is formed, and in many cases they are actually broken so that the adsorbed species are fragments of the original molecule. Thus, we speak of non-dissociative chemisorption if the gas molecule retains its integrity on the surface, and dissociative chemisorption if it does not. Examples of non-dissociative chemisorption are :

CO on (111) Ni [see (I) and (II) below]

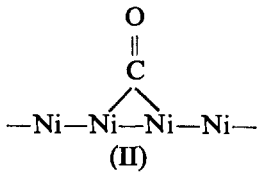
C_2H_4 on Fe and Cu

C_6H_6 on Ni

It is not however easy to know the adsorption geometry, For CO on Ni, linear (I), and bridged (II) forms are possible.



(I)



(II)

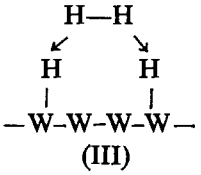
Examples of dissociative chemisorption are :

H_2 on (100) W [see (III) below]

CO on Mo

O_2 on most transition metals

N_2 on V



(III)

Chemisorption forces are quite different from those causing physisorption, and the Van der Waals attraction is insgnificant in determining the minimum in the potential energy curve. This minimum, and therefore the surface bond length, and the chemisorption binding energy, are determined by factors similar to those determining bond lengths, and bond dissociation energies in simple molecules. only the fact that the surface bond is formed between a macroscopic system (the solid), and a microscopic system (the adsorbed species), and can involve a very large number of electrons, might obscure this essential similarity.

Chemisorption binding energies, i.e., surface bond dissociation energies, like those of other chemical bonds, span a wide range, and include* :

*Binding energies depend on the crystal face, and on the adsorption site and geometry. The latter is not often known experimentally. Experiments with films yield an average over several crystal faces.

D (nickel-CO) 176 kJ mol^{-1}
D (vanadium-N) 795 kJ mol^{-1}
D (iron-N) 545 kJ mol^{-1}
} Films
D ((110) Fe-H) 268 kJ mol^{-1}

Chemisorption is important in many areas of Chemical Physics; in heterogeneous, catalysis, corrosion, and electrochemistry for example. In catalysis, chemisorption of at least one of the reactants is an essential step by which the solid surface provides new reaction paths not available in the homogeneous gas phase. The rate of the slowest step in the reaction by such a new path may be faster than that of the slowest step in the homogeneous reaction. If it is, the solid catalyzes the reaction.

Some important catalyzed reactions are :

$$N_2 + 3H_2 \xrightarrow{\text{Fe (450°C)}} 2NH_3 \text{ (ammonia synthesis)}$$

$$nCo + (2n+1)\,H_2 \xrightarrow{\text{Co (200°C)}} C_nH_{2n+2} + nH_2O \text{ (water gas reaction)}$$

$$C_nH_{2n} + H_3 \xrightarrow{\text{Pt (200°C)}} C_nH_{2n+2} \text{ (hydrogenation of olefins)}$$

The synthesis of ammonia in the homogeneous gas phase does not proceed at an appreciable rate because of the large activation barrier due to the need to dissociate the N_2 molecule [$D(N_2) = 941$ kJ mol^{-1}]. On an iron catalyst, the iron-N surface bond is strong enough to dissociate N_2, and this activation barrier is absent. But the iron-N surface bond is not so strong as to remove the nitrogen from further reaction with hydrogen (hydrogenation), and therefore to replace one large activation barrier by another. On the other hand, this is exactly the situation on vanadium, and with this metal there is no worthwhile catalysis of the ammonia synthesis.

There are two parts to theoretical studies of chemisorption :

(a) Statics. This is the determination of the equilibrium situation; bond lengths and energies, the adsorption geometry etc. I call this chemisorption theory.

(b) Dynamics. This is the study of molecular rate processes on solid surfaces, and of probe dynamics ; the rates of adsorption, chemical reactions, particle scattering, etc.

Dynamics is by far the larger part, but of course, by studying statics, we acquire an essential input into dynamical calculations.

Chemisorption theory proceeds at quantitative, semi-empirical, and qualitative levels. At the quantitative level, the first goal is to develop theoretical models of adsorbate/substrate systems which are suitable for the calculation of the equilibrium positions of all the nuclei, the ground-state energy, and the elementary

excitations. This goal is difficult to attain. It is a large-scale computing task, and the *a priori* geometry prediction is particularly hard to achieve over the wide range of chemisorption systems of practical importance. Because of this, many investigations determine the electronic structure, and some elementary excitations, for a single assumed nuclear geometry. But there are some notable exceptions which I shall mention in § 4.

Work at the semi-empirical level seeks to avoid the huge computer task of the fully quantitative approach by judicious use of numerical approximations, and experimental data. But semi-empirical theories are intended to be useful, and valid approximations to specific quantitative models, and because of this, I shall confine myself to the *primary* theoretical models in chemisorption theory.

Qualitative work in chemisorption theory is directed towards "understanding" the chemisorption bond, to developing useful concepts in quantum chemistry at solid surfaces, and to correlating and explaining experimental data. It is at this level that Anderson's[1] Hamiltonian has been valuable[2].

We are concerned in chemisorption theory to a large extent with molecular orbital (MO) schemes, and I mention here the more important MO schemes in use in the quantum chemistry of molecules and solids. The Hartree-Fock (HF) theory in its single configuration form is a well-known approximation, but there exist two *exact* MO schemes too. First there is the Kohn-Sham[11] scheme giving the exact ground-state energy, and the electron density by formulae involving sums on "occupied orbitals" rather like those of the HF model. On the other hand, the exact ionization, and affinity levels are the "orbital energies" of a completely different potential from that in the Kohn-Sham (KS) equations; they are the energies of *Dyson orbitals* of a non-Hermitian eigenvalue problem, and an energy-dependent potential. This is the dynamic Hartree-Fock (DHF) scheme, and in this scheme, the formulae for the ground-state energy, and the electron density involve sums on Dyson orbitals with however, non-integral occupation numbers. I give more details in § 3.

Although there are difficult problems still to be overcome in the theory of the equilibrium properties of chemisorption systems, firstly kinetics, and secondly, reaction dynamics are at the heart of Surface Chemistry. In kinetics we are concerned with macroscopic quantities like the rate of a reaction per unit area of the catalyst, the dependence of this rate on the temperature, on the pressures of the reactants, and so on. In reaction dynamics, we are concerned with the behaviour of single reactant molecules in their encounters with the catalyst, with adsorbed species, and so on. Because they are so heavy, it is usually possible to treat the translational motions of the reactants classically, but the other degrees of freedom, and of course the electronic motion, have to be treated by quantum mechanics. Among the simplest dynamical processes on solid surfaces we note :

(a) Sticking. For example the rate of adsorption of a reactive species like H atoms by a solid metal :

$$\text{Solid} + \text{H} \longrightarrow (\text{Solid-H})^*$$

the star (*) indicating an excited state.

(b) Flash desorption. For example the rate of desorption of a rare gas atom like He from a solid when the solid is suddenly heated :

$$(\text{Solid-He})^* \longrightarrow \text{Solid} + \text{He}.$$

If it is to stick on a solid, a gas atom must lose at least its kinetic energy, otherwise it will bounce back (inelastically perhaps) into the gas phase (Fig. 2). The required energy may be lost by exciting the vibrations of the solid (loss to phonons) or by exciting the electron system (loss to electrons), or by both. A light atom like hydrogen connot easily lose its kinetic energy to phonons in a collision with the surface of metal composed of much heavier atoms (think of the fairground coconut shy), and in this example, energy loss to the electrons is the likely mechanism for sticking. The fact that the H atom is a reactive species forming a strong chemisorption bond under equilibrium conditions also helps the electron loss mechanism: very profound changes in the electron distribution between the atom and the solid must occur during the collision *if the electronic motion is to remain unexcited.* By contrast, the flash desorption (Fig. 3) of a physically adsorbed rare gas atom like He is likely to be driven by energy transfer from the thermally excited phonon system; physisorption involves only small changes in the distribution of electrons between the atom and the solid.

I shall give some details of the *full quantum mechanical approach* to these dynamical processes later, but I mention here an even simpler dynamical process on a solid surface, namely the electron transfer between the solid and a fast (500 eV) atom or ion reflected from it. The translational motion of the fast gas particle can be treated classically, and this determines a time-dependent perturbation of the electron system whose quantum state therefore evolves in time through the collision. By following this time evolution with Schrödinger's

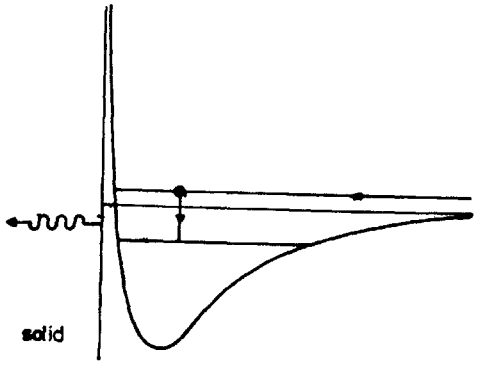


FIG. 2. Sticking. The gas atom leses energy to the solid and falls into a bound state.

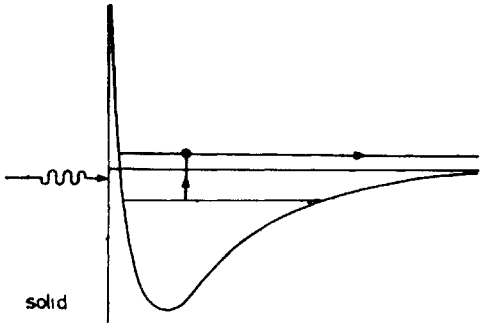


FIG. 3. Thermal desorption. The adsorbed atom gains energy from the hot solid and is excited into an unbound state.

time equation, the probability of electron transfer can be computed[3–5]. The probability of excitation of the gas atom in the process can also be obtained[6].

2. UNDERSTANDING THE CHEMISORPTION BOND

The traditional attitude in chemistry is that chemical bonds can be understood at the level of simple orbital approximations, and a knowledge of the electronic structures of atoms at this level is sufficient to understand how stable molecules can be formed, and a similar knowledge of the electronic structures of molecules can tell us how molecules can react. More recently the role of "*frontier orbitals*" has been emphasized in making predictions about reaction mechanisms[7]. I now show how the concepts of frontier orbital theory are generalized in chemisorption theory where one of the partners in the bond (the solid) is a macroscopic system with a nearly continuous spectrum of MO's and energy levels[2,8].

2.1. Generalized frontier orbital theory

I consider the interaction of ethene with the (001) surface of aluminium, and ask the question : Knowing the electronic structures (MO's and energy levels) of ethene and (001) Al, can we decide if ethene will chemisorb on (001) Al ?

First we compare the orbital energies of electrons in ethene and aluminium (Fig. 4). The Fermi level of Al which separates occupied and unoccupied levels for electrons in the metal, lies between the Highest Occupied Molecular Orbital (HOMO), and the Lowest Unoccupied Molecular Orbital (LUMO) of ethene. A chemical bond between ethene and the metal can be formed by an electron in the ethene HOMO hopping to the metal into a normally unoccupied MO of aluminium above the Fermi level, ϵ_F, or by an electron hopping from an MO of aluminium below ϵ_F into the ethene LUMO. Consequently we write an approximete many-electron wavefunction ψ for the system by mixing the above *Charge-transfer states* with the neutral ground state of the non-interacting system;

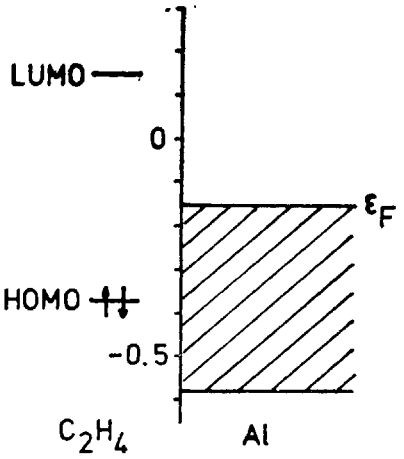


FIG. 4. The energy levels of ethene and aluminium metal.

$$\psi = N_0\psi_0 + \sum_{K = \text{occupied}} A_K\psi_K\ (C_2H_4^-, Al^+) + \sum_{K = \text{vacant}} C_K\psi_K\ (C_2H_4^+, Al^-)$$

We then use the variation theorem to estimate the ground-state energy. This leads to an expression for the chemisorption binding energy D (positive for stability) which through second-order terms is

$$D = 2\int_{-\infty}^{\epsilon_F} d\epsilon \frac{w_{LUMO}(\epsilon)}{\epsilon_{LUMO} - \epsilon} + 2\int_{\epsilon_F}^{0} d\epsilon \frac{w_{HOMO}(\epsilon)}{\epsilon - \epsilon_{HOMO}} \qquad \ldots (2.2)$$

Here w_{HOMO} and w_{LUMO} are the *spectral densities* of the interactions of the ethene frontier orbitals with the Mo's of the metal. I assume that w_{HOMO} and w_{LUMO} are proportional to the spectral densities of the overlaps of the respective frontier orbitals with the metal Mo's :

$$w_{HOMO}(\epsilon) \propto \rho_{HOMO}(\epsilon) = \sum_K |\langle HOMO|K\rangle|^2 \delta(\epsilon - \epsilon K)$$

$$w_{LUMO}(\epsilon) \propto \rho_{LUMO}(\epsilon) = \sum_K |\langle LUMO|K\rangle|^2 \delta(\epsilon - \epsilon K) \qquad \ldots (2.3)$$

Both integrals on the right in (2.2) are positive, and both therefore contribute to stabilize the chemisorbed state. However the first term would contribute little if ρ_{LUMO} had little of its density in the occupied states of the metal (i.e., below ϵ_F), and the second term would contribute little if ρ_{HOMO} had little of its density in the unoccupied metal states. If both conditions were to hold, ethene would not chemisorb. Detailed computer calculations[2] using the Huckel MO theory (the tight binding approximation of solid state physics) show that for C_2H_4 on (001)Al in the adsorption geometry of Fig. 5, ρ_{LUMO} and ρ_{HOMO} have significant

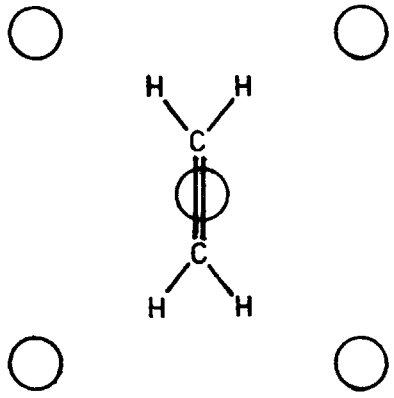


FIG. 5. C_2H_4 on (001) Al.

portions of their densities below and above ϵ_F respectively. Consequently both terms in (2.2) contribute significantly to D (Al (100) — C_2H_4), and we expect ethene to be chemisorbed, which it is in practice.

The above argument using ρ_{LUMO} and ρ_{HOMO} is essentially a symmetry argument like those introduced into organic reaction machanisms by Woodward and Hoffman[9], and Fukui[10]. Indeed, the argument I have given here applies as much to the cyclo-addition of ethene to a diene as to its chemisorption by aluminium. But for the cyclo-addition reaction we have a discrete, not a continuous spectrum of substrate MO's, and therefore ρ_{LUMO} and ρ_{HOMO} consist simply of δ-functions of various strengths, betweed 0 and 1, at the MO energies of the diene. If we calculate using Huckel MO theory we find that ρ_{LUMO} has only 11 per cent of its density in the occupied diene MO's and similarly ρ_{HOMO} has only 11 per cent of its density in the unoccupied diene MO's. Thus both integrals in (2.2) are small, and because of symmetry factors essentially, the cyclo-addition to form vinylcylobutane is not expected. In fact, according to Woodward and Hoffmann[9] the reaction is symmetry forbidden. By contrast, the symmetry factors for the chemisorption of C_2H_4 by (001) Al are not unfavourable because there exist in Al large numbers of MO's with energies near ϵ_F, and large amplitudes in the (001) surface, *and* with the right symmetries to interact with the C_2H_4 frontier orbitals.

3. Exact Molecular Orbital Schemes

As I have already mentioned, there are two exact, but very different MO schemes, the density functional (DF), and the dynamic Hartree-Fock (DHF) schemes.

The DF scheme gives the ground-state energy E_0, and the electron density $n(r)$ by solving self-consistently, the one-particle Kohu-Sham[11] equations which

have a *local* potential v_{eff} [n; r] which is, as indicated, a functional of the electron density. The equations are, in atomic units*

$$(-\tfrac{1}{2}\nabla^2 + v_{eff}[n;\mathbf{r}]\,\psi_\alpha(\mathbf{r}) = \epsilon_\alpha\,\psi_\alpha(\mathbf{r}) \qquad \ldots 3.1)$$

$$n(\mathbf{r}) = \sum_{\alpha=1}^{N} |\psi_\alpha(\mathbf{r})|^2$$

the sum being on the N lowest energy states for N electrons in the system. The difficulty is of course that v_{eff} is not known because all the complications of the N-electron problem are contained in it. The most commonly used approximation is the *local density approximation* (LDA) where

$$v_{eff}[n;\mathbf{r}] \simeq v_H(\mathbf{r}) + \frac{d}{dn}\epsilon_{xc}(n)\,n \qquad \ldots(3.2)$$

where v_H is the electrostatic or Hartree, potential, and $\epsilon_{xc}(n)$ is the exchange-correlation energy per electron of a homogeneous electron gas of density n. Separating the exchange energy

$$\epsilon_{xc}(n) = -\tfrac{3}{4}(3n/\pi)^{1/3} + \epsilon_c(n) \qquad \ldots(3.3)$$

where ϵ_c, the correlation energy, is some interpolation of the known high- and low-density results, for example Wigner's[12] interpolation

$$\epsilon_c(n) = -\frac{0.056\,n^{1/3}}{0.079 + n^{1/3}} \qquad \ldots(3.4)$$

although more recent interpolations do not give significantly different results. The formula for the ground-state energy E_0 in the LDA is

$$E_0 = N\sum_{\alpha=1}^{N}\epsilon_\alpha - \tfrac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})\,n(\mathbf{r}')}{\mathbf{r}-\mathbf{r}'} - \int d\mathbf{r}n(\mathbf{r})\,\{v_{xc}(\mathbf{r}) - \epsilon_{XC}(\mathbf{r})\} \qquad \ldots(3.5)$$

The *DF* scheme gives exact formulae for the ground-state energy E_0 and electron density $n(\mathbf{r})$, but it tells us nothing exactly about the elementary excitations or the ionization or affinity levels of the system. The *DHF* scheme does.

The dynamic Hartee-Fock theory (*DHF*) starts from the equation of motion of the single particle Green function

$$G(\mathbf{r}, t; \mathbf{r}', t') = -i\,\langle N|\,T\psi(\mathbf{r}, t)\,\psi^+(\mathbf{r}', t')\,|N\rangle \qquad \ldots(3.6)$$

where ψ^+ and ψ are creation and destruction Fermion field operators in the Heisenberg representation, T is Wick's time-ordering operator, and $|N>$ is the exact N-electron ground state. The Fourier time transform of G is

$$G(\mathbf{r}, \mathbf{r}'; \epsilon) = \int_{-\infty}^{+\infty} d\tau e^{i\epsilon\tau}\,G(\mathbf{r}, t; \mathbf{r}', t') \qquad \ldots(3.7)$$

*The energy unit is the Hartree; 1 Hartree = 27.21 eV = 2625 KJ mol^{-1}

where $\tau = t - t'$. There exists at every ϵ, a bi-orthogonal set of function $u_\alpha(\mathbf{r}; \epsilon)$, $\bar{u}_\alpha(\mathbf{r}; \epsilon)$ which diagonalize G;

$$G(\mathbf{r}, \mathbf{r}'; \epsilon) = \sum_\alpha u_\alpha(\mathbf{r}; \epsilon)\, \bar{u}_\alpha(\mathbf{r}'; \epsilon)/[\epsilon - E_\alpha(\epsilon)]$$

$$< \bar{u}_\alpha(\mathbf{r}; \epsilon) \mid G(\mathbf{r}, \mathbf{r}'; \epsilon) \mid u_\alpha(\mathbf{r}'; \epsilon) > = \delta_{\alpha\beta}/[\epsilon - E_\alpha(\epsilon)] \qquad ...(3.8)$$

These functions satisfy the non-Hermitian eigenvalue problem

$$[E_\alpha(\epsilon) - h(\mathbf{r})]\, u_\alpha(\mathbf{r}; \epsilon) - \int d\mathbf{r}' M(\mathbf{r}, \mathbf{r}'; \epsilon)\, u_\alpha(\mathbf{r}'; \epsilon) = 0$$

$$[E^*_\alpha(\epsilon) - h(\mathbf{r})]\, \bar{u}_\alpha(\mathbf{r}; \epsilon) - \int d\mathbf{r}' \bar{u}_\alpha(\mathbf{r}; \epsilon)\, M(\mathbf{r}', \mathbf{r}; \epsilon) = 0 \qquad ...(3.9)$$

where $h(\mathbf{r})$ is the Schrödinger operator for an electron moving in the field of ions, and M is the self-energy containing all the complications of the N-electron problem. *M is non-local.*

G has poles at energies ϵ_α satisfying

$$\epsilon_\alpha = E_\alpha(\epsilon_\alpha) \qquad ...(3.10)$$

with residues η_α, and the functions $u_\alpha(\mathbf{r}; \epsilon_\alpha)$ which satisfy equations (3.9) at these energies are known as *Dyson orbitals*. In terms of these orbitals, the electron density is

$$n(\mathbf{r}) = \sum_\alpha \eta_\alpha u_\alpha(\mathbf{r}; \epsilon_\alpha)\, \bar{u}_\alpha(\mathbf{r}; \epsilon_\alpha)$$

$$(\epsilon_\alpha < \epsilon_F) \qquad ...(3.11)$$

and the ground-state energy is

$$E_0 = \sum_\alpha \eta_\alpha[\epsilon_\alpha + h(\alpha, \alpha)]$$

$$(\epsilon_\alpha < \epsilon_F) \qquad ...(3.12)$$

where $h(\alpha, \alpha)$ is the diagonal element of $h(\mathbf{r})$ in the Dyson orbital representation. The poles ϵ_α of G are the exact ionization, and affinity levels of the N-electron system.

Equations (3.9) – (3.12) provide an exact *MO* scheme. The most commonly used approximation to it is the ordinary *HY* model in which M is energy-independent (but still non-local), and consequently the residues η_α are all unity, and also the Dyson orbitals degenerate to the *HF* orbitals. The self-energy has the well-known form

$$M_{HF}(\mathbf{r}, \mathbf{r}') = v_H(\mathbf{r})\, \delta(\mathbf{r} - \mathbf{r}') + v_X(\mathbf{r}, \mathbf{r}') \qquad ...(3.13)$$

where v_X is the non-local exchange potential

$$v_X(\mathbf{r}, \mathbf{r}') = -\sum_\alpha u_\alpha(\mathbf{r})\, u^*_\alpha(\mathbf{r}')/ \mid \mathbf{r} - \mathbf{r}' \mid$$

$$(\epsilon_\alpha < \epsilon_F) \qquad ...(3.14)$$

4. Practical Computations

Computations are performed using either :

4.1. Cluster models

Here the solid with a given exposed surface is modelled by a few atoms (perhaps as few as 5 for the (100) surface of a face-centred cubic metal), and this cluster, plus the adsorbed species is computed as a problem in ordinary quantum chemistry. As an example of this approach I mention Upton and Goddard[13] who used 20 Ni atoms to investigate H atom chemisorption by nickel in the HF approximation. A cluster as large as this contains the more important sites on (100), (110), (111) and (112) surfaces. The chemisorption binding energies, equilibrium surface bond lengths, and frequencies computed.

4.2. Embedded clusters

In small clusters, very few (one in Ni_{10}, two in Ni_{20}) atoms have even the nearest-neighbour environment of the real solid, and we must therefore receive computations on small clusters with caution. But chemisorption is often a spatially well-localized phenomenon, and we know that binding energies, together with bond lengths and vibration frequencies of adsorbed species can be computed accurately with small clusters; Ni_{20} is adequate for H atom chemisorption. Now quite generally, if one tries to describe the properties of a large system (H plus 10^{15} Ni atoms) by focussing on a small part of it (H-Ni_{10}), the fact that the small part is in communication with the rest of the system can be accounted for exactly in quantum mechanics by using an *effective* Hamiltonian to describe the small part, and ignoring the rest of the system completely. Examples of this procedure are widespread in Chemical Physics.

In chemisorption theory we *embed* a cluster calculation into the semi-infinite substrate by adding an *embedding self-enetgy* $M^E(\mathbf{r}, \mathbf{r}'; \epsilon)$ to the cluster Hamiltonian H^C to define the effective Hamiltonian for electrons in the cluster

$$H_{eff} = H^C + M^E(\mathbf{r}, \mathbf{r}'; \epsilon) \qquad \ldots(4.1)$$

As indicated, M^E non-local, and energy-dependent, the same as H^C will be if we used the DHF theory for the cluster calculation. For a large cluster, M^E becomes a property of the semi-infinite substrate, and ceases to depend on the adsorbed species. In this limit its calculation is simplified, and its role is to bring the electronic structure of the bare cluster (no adsorbed species) to that of the same cluster of atoms in the surface of the semi-infinite substrate, i.e., to embed the substrate cluster, *without the adsorbed species*, exactly. Chemisorption disturbs this exact embedding of course, but the disturbance is small if chemisorption is spatially localized, and in any case it goes to zero with increasing cluster size.

There are some technical problems still to be overcome (e.g., dealing with possible poles in $(\epsilon - \mathrm{H}_{eff})^{-1}$ close to ϵ_F) before this embedding scheme can be generally used, but simple chemisorption systems have been successfully handled

this way[14-16], and many studies of single atoms, and diatomic molecules on "jellium" adopt this approach.

4.3. Slabs

For many chemisorption systems, the adsorbed species can form an ordered overlayer, with or without reconstruction of the solid surface, so that there is still a 2-dimensional translational symmetry specified by the *unit mesh* of the *surface net*. In this case, it is advantageous to consider a slab of the solid with ordered overlayers of the adsorbate on both surfaces, because this gives a 2-dimensional crystal with however a large unit cell since it extends right through the slab (Fig. 6). The large number of electrons in the unit cell limits the number of layers of the solid which can be included in the computation, but the method of proceeding is well-known whether one uses basis sets which are (i) atomic orbitals, (ii) plane waves, (iii) mixtures of both, and whether one uses the LD or the HF approximation, and an atomic orbital (AO) basis set. I mention some details of the approach using the HF approximation and an atomic orbital (AO) basis set[17,18] since I have some experience with it.

The MO's for a periodic system are expressed as linear combinations of tight-binding basis functions

$$\psi_\mu(\mathbf{k};\mathbf{r}) = \sum_i \phi_i(\mathbf{k};\mathbf{r})\, C_{i\mu}(\mathbf{k})$$

$$\phi_i(\mathbf{k};\mathbf{r}) = N^{-1/2} \sum_l \exp i\mathbf{k}.(\mathbf{l})\, u_i\,(\mathbf{r} - \mathbf{l} - s_i) \qquad \ldots(4.2)$$

where u_i is the ith AO on the atom at s_i in the unit cell at $\mathbf{l}$, and $\mathbf{k}$ is a wavevector in the 2-dimensional Brillouin zone of the surface net. ϕ_i is a Bloch sum. The coefficients $C_{i\mu}(\mathbf{k})$ in (4.2) are obtained by solving the matrix eigenvalue problem

$$\mathbf{F}(\mathbf{k})\,\mathbf{C}(\mathbf{k}) = \mathbf{S}(\mathbf{k})\,\mathbf{C}(\mathbf{k})\,\epsilon(\mathbf{k}) \qquad \ldots(4.3)$$

for every $\mathbf{k}$. For closed-shell systems in the HF approximation

$$F_{ij}(\mathbf{k}) = h_{ij}(\mathbf{k}) + \sum_{m,n} B^{-1} \int_B \mathbf{dk}\, \{J_{ijmn}(\mathbf{k},\mathbf{k}) - \tfrac{1}{2}K_{ijmn}(\mathbf{k},\mathbf{k}')\}\, P_{mn}(\mathbf{k}') \qquad \ldots(4.4)$$

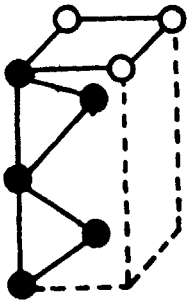


FIG. 6. The unit cell (0 atoms) and surface unit mesh of a 5-layer slab of a body-centred cubic metal with the (001) surfaces exposed.

Here h, J and k refer to the core Hamiltonian, the coulomb, and the exchange terms respectively, B is the area of the surface Brillouin zone, and $P(\mathbf{k})$ is the density matrix with elements defined on the basis set $\{\phi_i\}$ by

$$P_{ij}(\mathbf{k}) = 2 \sum_{\mu=occ} C^*_{i\mu}(\mathbf{k})\, C_{j\mu}(\mathbf{k}) \qquad \ldots(4.5)$$

the sum on μ being on the occupied orbitals ψ_μ. We note the usual *HF* self-consistency problem because we have to solve (4.3) to calculate $P(\mathbf{k})$ from (4.5), and we need $P(\mathbf{k})$ *for all* $\mathbf{k}$ to define $F(\mathbf{k})$. The total energy is given by

$$E_0 = \tfrac{1}{2}B^{-1} \int d\mathbf{k}\ \text{Trace}\ \mathbf{P}(\mathbf{k})\ \{\mathbf{F}(\mathbf{k}) + \mathbf{h}(\mathbf{k})\} \qquad \ldots(4.6)$$

Because of the long range of the Coulomb potential, there are important numerical problems connected both with the construction of F and with the evaluation of the total energy[19], but these need not concern us here, I simply remark that a comprehensive, well-documented and flexible computer program exists in the *UK* for large-scale *HF* computations on periodic systems. It is called CRYSTAL, and it began life at Turin (Italy) with the quantum chemistry group there. Results for *H*-(0001) Be using a 3-layer slab of Be (H—Be_3—H) have recently appeared in the literature[30], but tests have been made for several other systems. The results indicate that the *HF* model with small basis set of Gussian orbitals on each atom gives reliable *a priori* predictions of the adsorption geometry, with bond lenghts accurate to 0.005 *nm*, on non-metals certainly, and probably on metals too.

Many slab calculations using the *LD* approximation have been published which make various approximations to ease the computational task so that transition-metal substrates can be investigated. Much of this work concentrates on the spectrum of Kohn-Sham eigenvalues, and on the charge density, but neglects the total energy, and with it, the geometry optimization problem because total energies are unreliable due to the approximations made over and above the LD approximation. Among recent calculations of this sort I mention two :

(i) $c(2 \times 2)$ Cl on a 3-layer slab of (001) Ag using a Gaussian orbital basis, a Gaussian basis set for fitting $n(\mathbf{r})$ and $v_{eff}(\mathbf{r})$, and Wigner's[12] formula for ϵ_C[21].

(ii) monolayer Au on a 5-layer slab of (001) Pt using LAPW's (linearized augmented plane waves), touching muffin tins for the potential and Hedin and Lundqvist's[22] formula for ϵ_C[23].

My experience with the density functional scheme for small molecules[24] is that the 3-dimensional numerical integrations required to calculate the matrix elements of v_{eff} are difficult to perform with high numerical accuracy because of the rapid spatial variations of the Kohn-Sham wavefunctions both for the core electrons themselves, and for the valence electrons in the core region. This is why the total energy is difficult to compute with sufficient accuracy for *a priori*

geometry predictions. To avoid this difficulty (which is not present in the HF model because there, the integrals can be reduced analytically to 1-dimensional numerical integrations), there has been a move recently towards the use of *accurate* pseudopotentials, and pseudo-wavefunctions so that there are no core wavefunctions, and no rapid spatial variations of the valence (pseudo) wavefunctions in the core region. As an example of this approach I, mention the *ab initio* computations of the ground-state properties of Cl overlayers on (111) *Si* and (111) *Ge* using 6-layer slabs of substrate ($Cl\text{-}Si_6\text{-}Cl$, and $Cl\text{-}Ge_6\text{-}Cl$), the LD approximation in conjunction with accurate pseudopotentials, and a Gaussian orbital basis[25]. Surface bond lengths agree with experimental SEXAFS results to 0.002 A.U.

4.4. Jelliums

The jellium (Je) is a well-defined theoretical model. The positive ions of the solid are smeared out into a uniform charge distribution terminating abruptly at the surface. The electrons move in the electrostatic potential of this uniform background, and it is customory to treat their mutual interactions in the *LD* approximation. This material is a useful model for real solids if band structure effects (i.e., crystallinity), and core electrons are of secondary importance in chemisorption. It is therefore an adequate starting point for simple metals where band gaps are small (e.g., Na, Mg, Al), but is quite inadequate for surface chemistry which is intimately concerned with the adsorption geometry, and with local details rather than broad features, of the electron distribution. I remark however, that these important points can be taken into account by embedding a cluster as described in § 4.2. The great advantage of the jellium substrate is that the chemisorption of simple atoms, and molecules (H, O, H_2) can be computed essentially exactly in the *LD* approximation[26,27]. It has also been used with considerable success to begin the study of some dynamical processes[28].

5. Approximate Theories

The accurate computation of theoretical models which are adequate for the *ab initio* study of chemisorption poses a computing task which lies beyond the reach of most Institutions even for atomic adsorbates. Very few adsorbed molecules can be handled anywhere. Consequently, to begin to study systems of interest in catalysis, approximate methods have to be used. Among the most successful is the "Effective-medium Theory of Chemical Binding[29,30], "but I must remark that in its simplest form, which I give here, a given atom chemisorbs with the *same binding energy on all metals.*

The basic idea is to approximate $D(\mathbf{R})$, the binding energy of an atom to a substrate (another atom, or in our case a solid surface) when the atom is at $\mathbf{R}$, by the heat of solution H^{homo} of the atom in a jellium of (uniform) electron density $n_0(\mathbf{R})$, the electron density of the bare unperturbed substrate at the atom's position $\mathbf{R}$, i.e.

$$D(\mathbf{R}) \simeq H^{\text{homo}}(n_0(\mathbf{R})).$$

Systematic refinement of this idea leads to

$$D(\mathbf{R}) \simeq H^{\text{homo}}(\bar{n}_0(\mathbf{R})) \qquad \ldots (5.1)$$

where $\bar{n}_0(\mathbf{R})$ is an average of the unperturbed substrate electron density, namely

$$\bar{n}_0(\mathbf{R}) = \int d\mathbf{r} n_0(\mathbf{r} - \mathbf{R})\, \Delta\phi(\mathbf{r} - \mathbf{R}) \qquad \ldots (5.2)$$

Equation (5.1) is the zero-order result. The first-order correction to it is

$$D^{(1)}(\mathbf{R}) = -\int d\mathbf{r}\phi_0(\mathbf{r})\, \Delta\rho(\mathbf{r} - \mathbf{R}) - \int d\mathbf{r}[n_0(\mathbf{r} - \mathbf{R}) - \bar{n}_0(\mathbf{R})]\, \Delta v(\mathbf{r} - \mathbf{R}) \qquad \ldots (5.3)$$

where $\phi 0$ is the substrate electrostatic potential, and $\Delta\phi(\mathbf{r})$, $\Delta\rho(\mathbf{r})$ and $\Delta v(\mathbf{R})$ have the following meanings :

For a homogeneous jellium with uniform electron density $n_0(\mathrm{R})$, the atom placed at $\mathbf{r} = 0$ induces an electrostatic potential $\Delta\phi(\mathbf{r})$, a charge denisty $\Delta\rho(\mathbf{r})$, and a one-electron potential $\Delta v(\mathbf{r})$.

This first-order correction can be approximated by a term proportional to $\bar{n}_0(\mathbf{R})$

$$D^{(1)}(\mathbf{R}) \simeq \alpha\bar{n}_0(\mathbf{R})$$

so that

$$D(\mathbf{R}) \simeq H^{\text{homo}}(\bar{n}_0(\mathbf{R})) + \alpha\bar{n}_0(\mathbf{R}) = D[\bar{n}_0] \qquad \ldots (5.4)$$

$H^{\text{homo}}(n_0)$, the heat of solution of the atom in the homogeneous jellium has been calculated within the LD approximation for the atoms H to Ar by several authors[31], and from the details of these results, the function on the right in equation (5.4) can be obtained. I show it for the oxygen atom in Fig. 7[32]. It

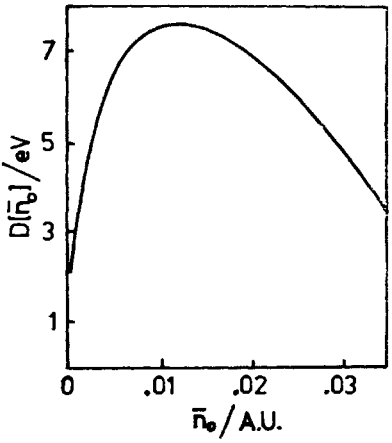


FIG. 7. The interaction energy of an oxygen atom with jellium according to equation (5.4). [Reference 32].

shows a maximum of 7.3 eV at 0.013 A.U. Outside a metal surface, an oxygen atom can always find this optimum electron density, and the corresponding position $\mathbf{R}_{eq}$ defined by

$$\bar{n}_0(\mathbf{R}_{eq}) = 0.013 \qquad \ldots(5.5)$$

gives the adsorption geometry. The chemisorption binding energy is simply the maximum value of $D[n_0]$, namely 7.3 eV. According to this simple theory, it is the same for all metals only the adsorption geometry determined by solving equation (5.5) can be different.

Experimental values of the binding energy of oxygen atoms to metals of the first transition series Ti to Cu apparently lie between 4.9 and 7.9 eV but they are not well-established quantities.

Refinements to the above scheme to differentiate one metal from another have recently been published[33], but I do not have space to discuss them here. I only remark that theoretical schemes which produce numbers for chemisorption systems of practical importance *must* produce reliable numbeas, otherwise they are useless.

6. Model Hamiltonians

Theoretical models designed to yield numbers, either to compare with experiment, or to be predictive, are at the core of chemisorption theory. But it is, in addition, very useful, particularly in the early stages of the development of the subject, and whenever new adsorption/desorption phenomena are being examined, to have a theoretical model which contains the essential features of the problem in by the simplest possible way. Anderson's model Hamiltonian[1] proposed originally to deal with a different problem, provides such a model because it can describe the formation of a chemical bond between a semi-infinite substrate with a continuum of itinerant electron states, and an atom with discrete localized ones in a simple way. Since its introduction into chemisorption theory by Grimley[34], Edwards and Newns[35], and Newns[36], it has been used very widely to exhibit many aspects of chemisorption by metals. I simply set down the Hamiltonian here for a one-electron atom interacting with a metal.

Let $\{\phi_A, \phi_K\}$ be a basis set consisting of the adatom orbital ϕ_A, and the set $\{\phi_K\}$ of metal orbitals. It is convenient to use the formalism of second quantization where the Hamiltonian is a function of Heisenberg operators $a_{i\sigma}, a_{i\sigma}^{+}$ $(i = A,K)$, where $a_{i\sigma}$ destroys an electron with spin σ ($\sigma = \uparrow$ or $\downarrow$) in the orbital ϕ_i. $a_{i\sigma}^{+}$ is the Hermitian adjoint, and is the corresponding destruction operator if the basis is orthogonal which is what is assumed in the Anderson model. Then

$$H = \sum_{\sigma} E_A n_{A\sigma} + J_A n_A \uparrow n_A \downarrow + \sum_{k,\sigma} \epsilon_k n_{k\sigma} + \sum_{k,\sigma} (V_{Ak} a_{A\sigma}^{+} a_{k\sigma} + V_{kA} a_{k\sigma}^{+} a_{A\sigma}) \qquad \ldots(6.1)$$

where $n_{A\sigma} = a^+_{A\sigma}\, a_{A\sigma}$ is the number operator for spin σ electrons in the orbital ϕ_A. The first term describes non-interacting electrons in the atom with energy E_A, the second is the Coulomb interaction between them, and together these two terms describe interacting electrons in the atomic orbital ϕ_A. The third term describes non-interacting electrons in the semi-infinite metal in orbitals ϕ_K with energies ϵ_K, and the fourth term couples the adsorbed atom, and the metal together by allowing them to share all the electrons. This sharing is described by $a^+_{K\sigma}\, a_{A\sigma}$ which takes a spin σ electron from the metal to the adsorbed atom, and by $a^+_{K\sigma} a_{A\sigma}$ which does the opposite. V_{AK} and V_{KA} moderate these charge transfers, and so govern the contributions of different metal orbitals ϕ_K to the surface bond.

The absence in Anderson's Hamiltonian (6.1) of any terms describing Coulomb interactions between electrons in the metal brings some unrealistic features to the model[2], which are partly removed in a different model introduced by Grimley and Pisani[14]. In this model, the states $|K>$ are tight-binding states constructed from a single atomic orbital per atom of the substrate, and such a model solid is called "cubium" if it has a cubic lattice. The atomic orbital basis set $\{\phi_A, \phi_M\ (M = \text{metal})\}$ is introduced to allow electron interactions to be extended from the adsorbed atom (A) in Anderson's model, to cover also its first shell of neighbours (B) in the substrate. Overlap among the atomic orbitals of the set $\{A + B\}$ is explicitly treated. The Hamiltonian is

$$H = \sum_{i,j,\sigma} a^+_{i\sigma} h_{ij} a_{j\sigma} + \tfrac{1}{2} \sum_{i,j,\sigma} a^+_i W^{\sigma}_{ij} a_{j\sigma}$$

$$(j\epsilon i,\ dbi) \qquad (i, j\epsilon A + B) \qquad \ldots(6.2)$$

where, as indicated, in the first term, j goes over i, and over the atoms directly bonded to i (dbi), and in the second, i and j go only over A and its first shell neighbours in the substrate (B). In equation (6.2)

$$h_{ij} = <i \mid \hat{h} \mid j> \qquad \ldots (6.3)$$

where $\hat{h}$ is the Schrödinger operator for an electron in the field of the ion cores, and

$$W_{ij} = \sum_{i',j',\sigma'} a^+_{i'\sigma'} <ii'\left|\frac{1}{r_{12}}\right|jj'> a_{j'\sigma'}$$

$$<ii'\left|\frac{1}{r_{12}}\right|jj'> = \int d\mathbf{r}_1 d\mathbf{r}_2\, \phi^*_i(\mathbf{r}_1)\, \phi^*_{i'}(\mathbf{r}_2)\, \phi_j(\mathbf{r}_1)\, \phi_{j'}(\mathbf{r}_2) / \mid \mathbf{r}_1 - \mathbf{r}_2 \mid$$

$$\ldots(6.4)$$

If i belongs to the non-orthogonal set $\{A + B\}$, the operator $a^+_{i\sigma}$ is not the creation operator for spin σ electrons in ϕ_i, it is simply the Hermitian adjoint of the destruction operator $a_{i\sigma}$.

Extending electron-electron interactions into the substrate like this, allows a more realistic charge distribution to develop near the chemisorbed atom. This is particularly important when ionic species form on the surface, for example with H atoms in Li metal[37].

7. Dynamics

Of course we are not able to give a proper microscopic discussion of any heterogeneous reaction, but the general way of proceeding is clear. What we need to do is to calculate R_{FI}, the rate of reactive transitions out of an initial state $|I>$ to a final state $|F>$. If the Hamiltonian is written

$$H = H_0 + V \qquad ...(7.1)$$

where H_0 describes the non-interacting reactants (the catalyst is a reactant in a state-to-state transition), V is the interaction between them, and $|I>$ and $|F>$ are eigenstates of H_0, then by Lippmann's generalization[38] of Ehrenfest's theorem

$$R_{FI} = \frac{2\pi}{\hbar} |<F|T|I>|^2 \delta(E_F - E_I) \qquad ...(7.2)$$

where the T-matrix is defined by

$$\begin{aligned} T &= V + VG^+V \qquad G^+ = (E + i0 - H)^{-1} \\ &= V + VG_0^+T \quad , \quad G_0^+ = (E + i0 - H_0)^{-1} \end{aligned} \qquad ... (7.3)$$

In a general chemical reaction, specifying the reactants specifies the *entrance channel* i, and specifying the products specifies the *exit channel* f ($A + BC \rightarrow AB + C$, and $A + BC \rightarrow AC + B$ have the same entrance channel but different f's). If the initial state is drawn from the canonical ensemble at temperature T, the transition rate from i to f can be written

$$R_{if} = \frac{kT}{\hbar} \int_0^\infty dE \exp(-E/kT) \frac{dY_{if}}{DE} Z_i(T) \qquad ...(7.4)$$

where $Y_{if}(E)$ is the probability of a transition to f from all states of energy E in i, and $Z_i(T)$ is the caniconal partition function for the reactants. We can write equation (7.4) in the form

$$R_F = \frac{kT}{h} \exp(-\Delta F^{\neq}/kT) \qquad ...(7.5)$$

and this defines $\Delta F^{\neq}$ the "free energy of activation from the entrance channel".

These equations are formal. To go beyond formalities, I consider the two simple processes which are fundamental to catalysis by solids; the rate of adsorption (sticking), and the rate of desorption of atoms at solid surfaces.

7.1. Sticking

If an atom or molecule is to stick, it must lose at least its kinetic energy in a collision with the surface. I assume that the energy is lost by exciting the electrons in the system. Whether or not this is the mechanism in any particular case it not easy to decide, but it is the most likely mechanism for H, H_2 and D_2 on transition metals. A feature of the electron-loss mechanism is that the fall in the sticking coefficient with increasing substrate temperature is expected to be very small, for the same reason, essentially, as the electronic contribution to the heat capacity of a metal is very small, namely Fermi statistics.

Consider a vessel of length b, one wall of which is the metal (Fig. 8), the other walls inert, and containing one gas atom. If we fix the gas atom at $\mathbf{R}$, and solve Schrödinger's equation for the electronic motion, we obtain the quasi-continuous sequence of adiabatic potential energy curves $E_n(\mathbf{R})$, where $n = 0,1,2,\ldots$ labels the electronic state; is the ground state, the others are excited states. By solving Schrödinger's equation for the motion of the gas atom nucleus on $E_n(\mathbf{R})$, we obtain states for the nuclear motion tabelled by α say, so that $|\, n,\alpha>$ and $E_{n\alpha}$ are the adiabatic states, and energies for the motion of the gas atom on the nth potential energy curve. If, in the course of a collision with the metal, the gas atom stays on the same potential energy curve, it can not stick, it can only reflect elastically. To stick, the atom must O move onto another potential energy curve with more energy in the electron system, and less in the nuclear motion.

I consider a situation in which the atom is initially in the state $|\, 0\alpha>$ with no electronic excitation, and with energy $E_{0\alpha}$ which is therefore the kinetic energy of the atom in the vessel. Because the electronic, and nuclear motions are not actually separable[39], the initial state $|\, 0,\alpha>$ is coupled to all other adiabatic states $|\, n, \beta>$, and therefore decays in time. From this decay, the sticking coefficient can be calculated.

The Hamiltonian has the form (7.1), and V causes the decay. The exact state at time t is $\Psi(t)$ satisfying

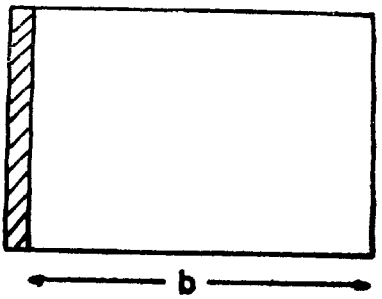


FIG 8. The gas vessel for calculating the sticking coefficient.

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \ (t > 0) \qquad \ldots(7.6)$$

and

$$\Psi(t) = \ | \ 0,\alpha > \text{ at } t = 0.$$

The probability to observe the initial state at time t is

$$| \ <\alpha, 0 \ | \ \Psi(t)> \ |^2 \text{ and}$$

$$<\alpha, 0 \ | \ \psi(t)> = <\alpha, 0 \ | \ U(t) \ | \ 0, \alpha>$$

where $U(t)$ is the evolution operator equal to $\exp(-iHt/\hbar)$ in our case. Hence

$$< \alpha,0 \ | \ \psi \ (t) > = -\frac{1}{\pi} \int_{-\infty}^{+\infty} d\epsilon \exp(-i\epsilon t) \ Im < \alpha,0 \ | \ G \ | \ 0,\alpha > \qquad \ldots(7.7)$$

where G is the Green operator

$$G \ (\epsilon) = (\epsilon + i0 - H)^{-1} \qquad \ldots (7.8)$$

These equations give the decay of the initial state; in general it decays through sticking, and through inelastic scattering. I now write down a simple model Hamiltonian describing sticking :

$$H_0 = \ | \ 0, \alpha > E_{0\alpha} < \alpha, 0 \ | \ + \sum_{\beta,n} | \ n, \beta > E_{n\beta} < \beta, n \ |$$

$$V = \sum_{\beta,n} (\ | \ 0, \alpha > W(0, \alpha; \beta, n) < \beta, n \ | \ + \ | \ n, \beta > W(n, \beta; \alpha, 0) < 0, \alpha \ | \qquad \ldots(7.9)$$

where $| \ n, \beta >$ specifies a *bound* state (β = bound) on the nth electronically excited potential energy curve, the electronic excitation consisting of *one* electron-hole pair (e-hp) (see Fig. 9).

From the Born-Oppenheimer system of linear equations[39] we identify

$$W(0, \alpha; \beta, n) = (\hbar^2/M) < \alpha \ | < \mu \ | \ \nabla_R \ | \ \nu > \Delta_R \ | \ \beta > \qquad \ldots(7.10)$$

where M is the mass of the gas atom, and $| \ \mu >$ and $| \ \nu >$ are one-electron states of the system with the gas atom at **R**. μ is the electron, ν is the hole (Fig. 9), and together they define the e-hp of the excited state $| \ n >$. Since the Hamiltonian (7.9) does not allow inelastic scattering (because β is confined to the bound states),

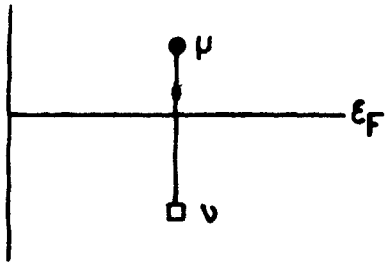


FIG. 9. One electron-hole pair. μ is the electron, ν is the hole.

the decay (7.7) is due entirely to sticking. Forming G from its definition in equation (7.8) we find

$$< \alpha, 0 \mid G \mid 0, \alpha > = (\epsilon + i0 - E_{0\alpha} - q_{0\alpha})^{-1} \qquad ...(7.11)$$

where

$$q_{0\alpha} = \sum_{\beta,n} \frac{|W(0, \alpha; \beta, n)|^2}{\epsilon + i0 - E_{n\beta}} = \alpha(\epsilon) - i\Gamma(\epsilon) \qquad ...(7.12)$$

is the self-energy of the state $\mid 0, \alpha >$ due to sticking.

Brivio and Grimley[40] have calculated the scalar product (7.7) in the quasi-particle approximation for a simple model of hydrogen chemisorption by a metal. The quasi-particle approximation consists of assuming that $< \alpha, 0 \mid G(z) \mid 0, \alpha >$ has a single pole in the lower-plane at $z_p = E_{0\alpha} - i\Gamma(E_{0\alpha})$, and in this case (7.7) reduces to

$$< \alpha, 0 \mid \Psi(t) > = \exp(-\Gamma(E_{0\alpha})\ t/\hbar \qquad ...(7.13)$$

The lifetime of the initial state is therefore

$$\tau = \hbar/2\Gamma(E_{0\alpha}) \qquad ...(7.14)$$

From the gas atom's kinetic energy $E_{0\alpha}$ we obtain τ_{coll}, the time between successive collisions of the gas atom with the metal

$$\tau_{\text{coll}} = (Mb^2/E_{0\alpha})^{1/2} \qquad ...(7.15)$$

and from (7.14) and (7.15), the sticking coefficient s is

$$s = \tau_{\text{coll}}/\tau \qquad ...(7.16)$$

Figure 10 shows some of the results[40]. The peak near 21 meV is due to a quantum mechanical transmission resonance of the hydrogen atom into the chemisorption well. I remark also that in the quasi-particle approximation $s \sim (E_{0\alpha})^{1/2}$ as $E_{0\alpha} \to 0$ as Fig. 10 shows, but the actual behaviour of s in this low energy limit requires a more accurate solution than this.

7.2. Thermal desorption

I assume that thermal desorption is driven by the substrate phonons not by the electrons, and examine the one-phonon desorption rate in the Golden Rule approximation for a simple theoretical model. The angle-resolved desorption flux $d\dot{N}/d\omega$, where ω is the solid angle, is an interesting quantity which is now being measured.

The essential features of the model are :

(i) The static gas-solid interaction potential describes a flat surface with a hard wall repulsion.

(ii) The movement of a surface atom of the substrate due to lattice vibrations causes a small area s of the hard wall round the atom to move with it.

(iii) Initial (bound), and final (unbound) states of the gas atom are described by WKB wavefunctions.

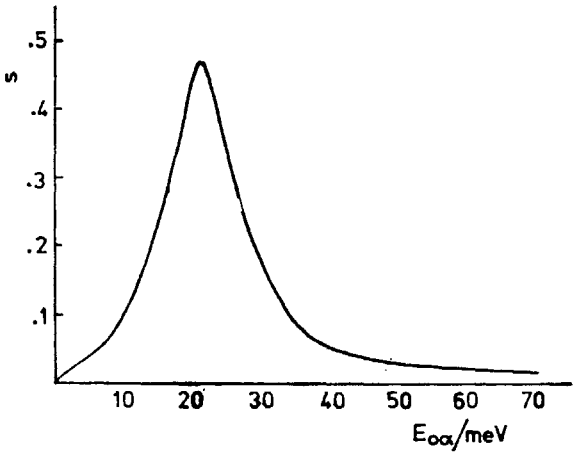


FIG. 10. Energy dependence of the sticking coefficient calculated for H atoms on a metal. $E_{0\alpha}$ is the kinetic energy.

(iv) The initial state of the system is drawn from the canonical ensemble at temperature T.

(v) Umklapp processes are neglected.
The Hamiltonian is

$$H = K_A + K_L + V(\mathbf{x}, \mathbf{u}_L) \qquad \ldots(7.17)$$

where K_A and K_L are kinetic energies of the gas atom A, and of the substrate lattice L, and V is the potential energy of the system when the gas atom is at $\mathbf{x}$, and the lattice atoms are displaced from their equilibrium positions. $\mathbf{u}_L$ is a multidimensional vector standing for the set $\{\mathbf{u}_L\}$ where $\mathbf{u}_L$ is the displacement of the atom at $\mathbf{l}$. I write (7.17) in the form

$$H = H_{\text{rigid}} + H_{\text{ph}} + V_{A-\text{ph}} \qquad \ldots(7.18)$$

where

$$H_{\text{rigid}} = K_A + V(\mathbf{x}, 0) \qquad (7.19)$$

is the Hamiltonian for the gas atom moving on the static atom-solid potential $V(\mathbf{x}, 0)$, i.e., the potential when the substrate atoms are clamped in their equilibrium positions,

$$H_{ph} = K_L + V(\infty, \mathbf{u}_L) \qquad \ldots(7.20)$$

is the Hamiltonian for the substrate lattice with the gas atom infinitely far from it, and V_{A-ph} is the atom-lattice interaction. In the harmonic approximation (7.20) is written

$$H_{ph} = \sum_{q,\sigma} \hbar\Omega_{q\sigma} b^{+}_{q\sigma} b_{q\sigma} \qquad \ldots(7.21)$$

where $(\mathbf{q},\sigma)$ are quantum numbers labelling the normal modes of frequencies $\Omega_{q\sigma}$. In a semi-infinite, crystal, $\mathbf{q} = (\mathbf{Q}, q_z)$ where $\mathbf{Q}$ is a 2-dimensional wavevector, and (q_z,σ) are the other labels which in simple cases we expect to be a perpendicular wavevector q_z, which may be complex if surface modes exist, and a mode index σ with three values. We expand $V(\mathbf{x}, \mathbf{u}_L)$ in a Taylor's series in $\mathbf{u}_L$ to find the first non-zero term in V_{A-ph}. It is the linear term

$$V_{A-ph} = \sum_{\mathbf{l}} \mathbf{u}_{\mathbf{l}} \cdot \nabla_{\mathbf{l}} V(\mathbf{x}, 0) \qquad \ldots(7.22)$$

Next we write $\mathbf{u}_{\mathbf{l}}$ in terms of the Boson operators. For a lattice with one atom per unit cell, N_Z layers parallel to the surface, and periodic boundary conditions over N meshes of the surface net

$$\mathbf{u}_{\mathbf{l}} = (NN_ZM_L)^{-1/2}\, \mathbf{e}_\sigma(l_z; \mathbf{q}) \exp(i\mathbf{Q}\cdot\mathbf{L}) \qquad \ldots(7.23)$$

where M_L is the mass of the lattice atoms, positions $\mathbf{l} = (\mathbf{L}, l_z)$ where l_z labels the layers from $l_z = 0$ at the surface, and $\mathbf{e}_\sigma$ is a unit vector specifying the direction of polarization of the mode $(\mathbf{q}, \sigma)$. In a semi-infinite crystal, the polarization depends on the l_z, the distance from the surface. Using (7.23) in (7.22), and introducing the Boson operators we can write

$$V_{A-ph} = \sum_{q,\sigma} g_{q\sigma}(\mathbf{x})\ (b^{+}_{q\sigma} + b_{q\sigma})$$

$$g_{q\sigma} = \left(\frac{\hbar}{2NN_zM_L\Omega_{q\sigma}}\right)^{1/2} \sum_{\mathbf{l}} \mathbf{e}_\sigma(l_z; \mathbf{q})\cdot\nabla_{\mathbf{l}} V(\mathbf{x}, 0) \exp(i\mathbf{Q}\cdot\mathbf{L}) \qquad \ldots(7.24)$$

Equations (7.18)-(7.24) specify the problem.

Initial, and final states $|\, I>$ and $|\, F>$ are eigenstates of H_0 where

$$H_0 = H_{\text{rigid}} + H_{\text{ph}}$$

and V_{A-ph} causes desorption. $|\, I>$ describes a bond state $|\, \alpha>$ of H_{rigid} with energy $\tilde{\epsilon}_\alpha$, and with n_i phonons in the solid. $|\, F>$ describes an unbound state $|\, f>$ of H_{rigid} with energy $\tilde{\epsilon}_f$, and with n_f phonons :

$$|\, I> = |\, \alpha>\, |\, n_i>\ ,\quad |\, F> = |\, f>\, |\, n_f>$$

From Lippmann's[38] generalization of Ehrenfest's theorem, the transition rate from $|\, I>$ to $|\, F>$ is

$$R_{Fi} = 2\pi/\hbar\ |\, <F\,|\, T_{A-ph}\,|\, I>\,|^2\, \delta(E_F - E_I)$$

where the T-matrix is

$$T = V_{A-ph} + V_{A-ph}\, G^{+}(E_I)\, V_{A-ph}$$

$$G^{+}(E) = (E + i0 - H)^{-1}$$

The Golden-Rule formula which I use is obtained with $T_{A-ph} \simeq V_{A-ph}$. If the initial state is drawn from the canonical ensemble at temperature T, the rate to $|\, F>$ is

$$R_F = (2\pi/\hbar) \sum_I \exp(-E_I/kT) \mid < F \mid T_{A-ph} \mid I > \mid^2 \delta(E_F - E_I) / \sum_I \exp(-E_I/kT)$$

and we recognize the denominator as the partition function. Summing on the final phonon state (which is not measured) gives the rate to the gas atom state $\mid f >$ irrespective of the final phonon state. This is the measured desorption rate R_f;

$$R_f = \sum_{n_f} R_F,$$

which determines the angle- and energy-resolved desorption flux

$$\frac{d^2\dot{N}}{d\omega d\tilde{\epsilon}_f} = \frac{\mathcal{V}}{(2\pi)^3} \cdot \frac{M}{\hbar^3} 2M\tilde{\epsilon}_f \cdot R_f \qquad \ldots(7.25)$$

at energy $\tilde{\epsilon}_f$ into unit solid angle at angle θ_f to the surface normal. In equation (7.25), $\mathcal{V}$ is the normalization volume for $\mid f >$, and M is the gas atom mass. The angle-resolved flux is

$$\frac{d\dot{N}}{d\omega} = \int_0^\infty d\tilde{\epsilon}_f \frac{d^2\dot{N}}{d\omega d\tilde{\epsilon}_f}$$

Skipping all further methematical details we find with assumptions (i) - (v)

$$R_f \sim \exp(-(\tilde{\epsilon}_f + V_0)/kT) \sum_\alpha \frac{[\tilde{\epsilon}_f \cos^2\theta_f (\tilde{\epsilon}_f \cos^2\theta_f + V_0)]^{1/2}}{\hbar\Omega_{f\alpha}} \times \rho_z(\Omega_{f\alpha}) \left(\frac{\alpha\epsilon}{a_\alpha}\right) \qquad \ldots(7.26)$$

where $\rho_z(\Omega)$ is a projection onto a surface atom of the solid of the phonon density of states:

$$\rho_s(\Omega) = \sum_{q,\sigma} \mid (e_{\sigma z}(0, \mathbf{q}) \mid^2 \delta(\Omega - \Omega_{q\sigma}) \qquad \ldots(7.27)$$

where $e_{\sigma z}(0, \mathbf{q})$ is the z-component (perpendicular to the surface) of the polarization vector of the mode $(\mathbf{q}, \sigma)$ on a surface atom. In equation (7.26), V_0 is the depth of the 1-dimensional static atom-solid potential $V(z, 0)$, ϵ_α are its bound state energies, a_α is the length of the classical trajectory of the state $\mid \alpha >$, and

$$\hbar\Omega_{f\alpha} = \tilde{\epsilon}_f \cos^2\theta_f + V_0 - \epsilon_\alpha \qquad \ldots(7.28)$$

is the energy increase of the adsorbed atom due to the adsorption of a phonon of frequency $\Omega_{f\alpha}$.

I note that it is impossible for (7.26) to lead to a $\cos\theta_f$ angular dependence such as is given by Kundsen's[41] arguments. Of course this is expected; I am dealing here with a completely non-equilibrium situation.

As an example of (7.26), suppose that thermal desorption is driven by surface phonos with

$$\rho_s(\Omega) \propto \Omega \quad , \quad 0 < \Omega < \Omega_{max} \qquad ...(7.29)$$

that $V(z, 0)$ has one bound state with $\epsilon_\alpha = \frac{1}{2}\hbar\Omega_{max}$, and that $V_0 = \hbar\Omega_{max}$. Then, for the angular dependence we find

$$R_f \sim [Y\cos^2\theta_f(Y\cos^2\theta_f + 1)]^{1/2},\ Y = \tilde{\epsilon}_f/\hbar\Omega_{max}$$

$$\frac{dN}{d\omega} \sim \int_0^{Y_m} dY\,[Y\cos^2\theta_f(Y\cos^2\theta_f + 1)]^{1/2}\exp(-Y\hbar\Omega_{max}/kT) \qquad ...(7.30)$$

$$Y_m = 1/2\cos^2\theta_f$$

In Fig. 11. I show the angle-dependence of the desorption flux normalized to unity at $\theta_f = 0$ (normal emission) for two temperatures; $T_2 = \hbar\Omega_{max}/k$ and $T_1 = \hbar\Omega_{max}/3k$. The flux goes through a maximum as θ_f increases because the upper limit of integration Y_m increases with θ_f, although the integrand itself decreases. Physically, this is due to the conservation of parallel momentum in desorption from the non-localized state on a flat surface. To eliminate this maximum, and therefore to get something looking more like $\cos\theta_f$, we need the bound state $|\alpha>$ to be near the top of the well, and the desorption temperature T to be rather low. However, I emphasize that the conditions I am considering here are special, a one-phonon mechanism, and an adsorbed layer so dilute that interactions between the adsorbed atoms are insignificant. The latter condition is so special as not to be attained easily in practice. Fortunately, it is possible to re-formulate the theory without it. This reformulation has similarities with the many-body theory of the photomission of electrons from adsorbate layers[42], but I do not have space to present it here. In any case no numerical results for the new theory are available yet.

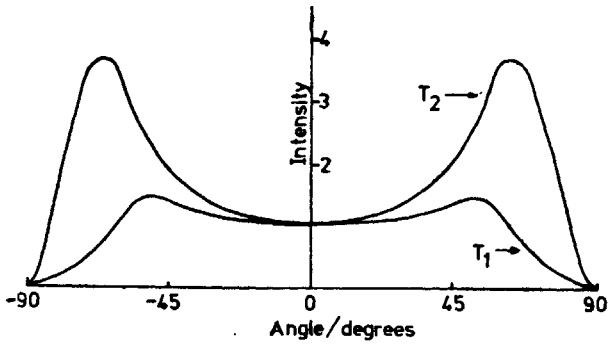


FIG. 11. The thermal desorption flux for the surface phonon mechanism as a function of angle to the surface normal for a flat adsorption potential with one bound state at $\epsilon_\alpha = \frac{1}{2}\hbar\Omega_{max}$. The well depth is $\hbar\Omega_{max}$, and the two temperatures are $T_1 = \frac{1}{3}\hbar\Omega_{max}/k$, $T_2 = \hbar\Omega_{max}/k$.

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