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T. B. Grimley

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Commentary on local densities of states, surface bonds and rate processes

BY T. B. GRIMLEY

Donnan Laboratories, University of Liverpool, P.O. Box 147,
Liverpool L69 3*BX*, *U.K.*

Although the main part of the title of this meeting is 'Studies of the surfaces of solids by electron spectroscopy', the papers presented also cover some of the wider aspects of these studies, and I wish to pursue some of these here. I remark first that most of the systems studied by surface-sensitive spectroscopies are not technologically important, or even interesting in their own right. What makes them important and interesting is that the solids studied are, or are related to, catalysts, and the adsorbates studied are reactants, products or intermediates in important catalytic reactions. Consequently I ask the question: what is the relevance to catalysis of studies of structure, and bonding at solid surfaces? From among the many answers that might be given, I select two.

(1) For many years now, chemists have believed that chemical bonds can be understood in terms of the electronic structures of the partners in the bond. Consequently, if the electronic structure of a solid surface could be described quantitatively (preferably in terms of molecular orbitals), it should be possible to understand its chemisorption properties, and perhaps its catalytic activity too. One way to present the electronic structure of a macroscopic object like a piece of metal with many millions of molecular orbitals is through the local density of states,

$$\rho(\boldsymbol{r},\epsilon) = \sum_{\mu} |\psi_{\mu}(\boldsymbol{r})|^2 \delta(\epsilon-\epsilon_{\mu}), \tag{1}$$

where ψ_μ and ϵ_μ are the molecular orbitals and their energies. Since (1) is defined at all points $\boldsymbol{r}$ inside, and outside the solid, it is more economical to form the projection $\rho_{\mathrm{g}}(\epsilon)$ of $\rho(\boldsymbol{r},\epsilon)$ on surface-localized orbitals ϕ_{g}, having the same symmetries (here labelled by g) as the valence orbitals on a particular adsorbate;

$$\rho_{\mathrm{g}}(\epsilon) = \sum_{\mu} |\langle \phi_{\mathrm{g}}(\boldsymbol{r}) | \psi_{\mu}(\boldsymbol{r}) \rangle|^2 \, \delta(\epsilon-\epsilon_{\mu}). \tag{2}$$

(2) Systematic experimental studies of adsorption geometry, surface-bond lengths and vibration frequencies provide information on a small portion of the ground-state electronically adiabatic potential-energy surface (g.s.e.a.p.e.s.) against which to test *ab initio* calculations. Linewidths tell us something about the mechanism (and efficiency) of energy exchange between the adsorbate, and the substrate, which, in 'stochastic trajectory' techniques for investigating gas–surface dynamics theoretically, determines the memory kernel, and the fluctuating force.

However, I do not pretend that the study of clean surfaces of solids, and of adsorbates, is anything more than the start of a much larger study of gas–surface dynamics. It is therefore useful on the one hand to remind ourselves of the enormous task ahead, and on the other to observe how relatively simple considerations have already thrown light on a central problem in catalysis by metals, that of promotors and poisons.

A solid catalyst can affect a chemical reaction in two important ways. (i) It can modify the g.s.e.a.p.e.s. so as to provide pathways not available in the homogeneous gas phase. The ammonia synthesis on an iron catalyst,

$$3H_2 + N_2 \xrightarrow{\text{Fe (400 °C)}} 2NH_3, \quad \Delta U = -101 \text{ kJ mol}^{-1},$$

is a well known example. In the gas phase the reaction is inhibited by the large activation barrier preventing the dissociation of N_2 ($D(N_2) = 941$ kJ mol^{-1}). This barrier is lowered by the Fe catalyst: $E^* = 30$, 20 and 3 kJ mol^{-1} on Fe (110), Fe (100) and Fe (111), respectively (Ertl *et al.* 1982). (ii) It can provide both a source and a sink so that the reacting species can gain or lose energy at critical points on the modified g.s.e.a.p.e.s.

The computation of the g.s.e.a.p.e.s. for the reaction with the catalyst nuclei clamped is therefore an important step towards understanding heterogeneous reactions, although it does not by any means tell us everything we need to put into a dynamical calculation.

When (ii) is not important, catalysis is investigated theoretically by trajectory analysis on the g.s.e.a.p.e.s. When (ii) is important, the situation is, in general, much more complex because it includes cases where the nuclear motion of the reacting species does not evolve on a single g.s.e.a.p.e.s.

Energy exchange can proceed via electrons, or via phonons, and it is in the former case that the nuclear motion does not evolve on a single electronically adiabatic potential-energy surface (e.a.p.e.s.). For the latter (energy exchange with phonons), the nuclear motion of the reacting species *does* evolve on a single e.a.p.e.s., and one can construct a theoretical model described by a Hamiltonian with linear and quadratic couplings of the reacting species to the substrate phonons:

$$H = K_{\mathrm{M}} + E_0(\boldsymbol{R}) + H_{\mathrm{ph}} + V_{\mathrm{M\text{-}ph}}, \tag{3}$$

where K_{M} is the kinetic energy of the reacting molecules whose positions are specified by the multi-dimensional vector $\boldsymbol{R}$, $E_0(\boldsymbol{R})$ is the g.s.e.a.p.e.s. with the substrate nuclei clamped, H_{ph} is the Hamiltonian for the substrate phonons, and $V_{\mathrm{M\text{-}ph}}$ is the coupling of the reacting molecules to the substrate vibrations. In terms of the displacements $U(\boldsymbol{l})$ of the substrate atoms from their equilibrium positions

$$V_{\mathrm{M\text{-}ph}} = \sum_{l} \lambda(\boldsymbol{l};\boldsymbol{R})\, U(\boldsymbol{l}) + \sum_{ll'} \kappa(\boldsymbol{l},\boldsymbol{l'};\boldsymbol{R})\, U(\boldsymbol{l})\, U(\boldsymbol{l'}), \tag{4}$$

where $\boldsymbol{l}$ specifies both the equilibrium position of an atom, and its x-, y-, and z-displacements.

However, if multi-phonon processes are important (and this will generally be the case) it is better to solve for the substrate phonons in the presence of the reacting molecules at $\boldsymbol{R}$. Let $\boldsymbol{x}$ stand for the normal coordinates of the substrate vibrations when no reacting molecules are present. Then (3) may be written in the form

$$H = K_{\mathrm{M}}(\boldsymbol{R}) + E_0(\boldsymbol{R}) + H_{\mathrm{ph}}(\boldsymbol{x}) + V_{\mathrm{M\text{-}ph}}(\boldsymbol{R},\boldsymbol{x}), \tag{5}$$

where, as before, $V_{\mathrm{M\text{-}ph}}$ contains linear and quadratic coupling of the reacting molecules to the substrate phonons. The adiabatic equation for the substrate phonons in the presence of the reacting molecules at $\boldsymbol{R}$ is

$$[H_{\mathrm{ph}}(\boldsymbol{x}) + V_{\mathrm{M\text{-}ph}}(\boldsymbol{R},\boldsymbol{x}) - U_n(\boldsymbol{R})]\, \phi_n(\boldsymbol{x};\boldsymbol{R}) = 0, \tag{6}$$

where $U_n(\boldsymbol{R})$ is the energy of the nth phonon state $\phi_n(\boldsymbol{x};\boldsymbol{R})$ with the molecules at $\boldsymbol{R}$.

We expand the exact state $\chi(\boldsymbol{R},\boldsymbol{x})$ of the coupled system, reacting molecules on the vibrating g.s.e.a.p.e.s., as

$$\chi(\boldsymbol{R},\boldsymbol{x}) = \sum_n \phi_n(\boldsymbol{x};\boldsymbol{R})\,\psi_n(\boldsymbol{R}) \tag{7}$$

and so arrive at a system of coupled equations for the ψ_n:

$$[K_\mathrm{M}+E_0(\boldsymbol{R})+U_n(\boldsymbol{R})-E]\,\psi_n(\boldsymbol{R}) = -\sum_m C_{nm}(\boldsymbol{R})\,\psi_m(\boldsymbol{R}), \tag{8}$$

$$C_{nm}(\boldsymbol{R}) = \sum_A (\hbar^2/M_\mathrm{A})\,\langle n|\nabla_\mathrm{A}|m\rangle\,\nabla_\mathrm{A}+\langle n|K_\mathrm{M}|m\rangle, \tag{9}$$

where M_A is the mass of atom A in the reacting molecules, and ∇_A is the gradient operator with respect to the position of atom A. In (8) and (9), the matrix elements are taken over the phonon coordinates:

$$\left.\begin{aligned}\langle n|\nabla_\mathrm{A}|m\rangle &= \int \mathrm{d}\boldsymbol{x}\,\phi_n^*(\boldsymbol{x};\boldsymbol{R})\,\nabla_\mathrm{A}\,\phi_m(\boldsymbol{x};\boldsymbol{R}),\\ \langle n|K_\mathrm{M}|m\rangle &= \int \mathrm{d}\boldsymbol{x}\,\phi_n^*(\boldsymbol{x};\boldsymbol{R})\,K_\mathrm{M}\,\phi_m(\boldsymbol{x};\boldsymbol{R}).\end{aligned}\right\} \tag{10}$$

Neglecting all couplings C_{nm}, the nuclear motion of the reacting molecules evolves on the single potential-energy surface

$$E_{0n}(\boldsymbol{R}) = E_0(\boldsymbol{R})+U_n(\boldsymbol{R}) \tag{11}$$

obtained from $E_0(\boldsymbol{R})$, the g.s.e.a.p.e.s., by adding the energy of the nth phonon state of the substrate with the reacting molecules at $\boldsymbol{R}$. This is an $\boldsymbol{R}$-dependent addition because the phonon frequencies depend on where the reacting molecules are. The phonon state will usually be drawn from the canonical ensemble, in which case $U_n(\boldsymbol{R})$ is replaced by a thermally averaged potential.

It is difficult to imagine a case where all atoms in the reacting molecules are moving so slowly that the C_{nm} can be neglected and therefore I note that, in a formal way, the effect of the C_{nm} in (8) is to add to $E_{0n}(\boldsymbol{R})$ in (11), a self-energy, or optical potential for reacting species near the substrate. This optical potential will appear, for example, in the dynamics of scattering from an initial state ψ_n of energy E specifying the reacting molecules coming onto the catalyst on the potential energy surface $E_{0n}(\boldsymbol{R})$.

A heterogeneous reaction that evolves on a single potential-energy surface, like a gas-phase reaction, proceeds at constant energy of the reacting molecules. So, an exothermic reaction must yield products with high translational or vibrational energies. It cannot yield electronically excited species. If the ammonia synthesis proceeded in such a fashion, each NH_3 molecule would be produced with *ca.* 50 kJ mol^{-1} of translational–vibrational energy. Similarly, for the methane synthesis

$$3H_2+CO \xrightarrow{\text{Co (200 °C)}} CH_4+H_2O, \quad \Delta U = -206\ \text{kJ mol}^{-1},$$

the products would share the 206 kJ mol^{-1} in their translations and vibrations. Such hot products are not, as far as I know, observed, and we conclude that energy loss from the reacting molecules to the catalyst is an essential feature.

Reactions that give gaseous products *can* theoretically proceed without energy loss from the reacting molecules to the substrate. The best known example of a reaction that does not proceed unless there is energy loss, is the chemisorption process itself, namely the sticking of a molecule on a solid surface. Without energy loss, the incoming molecule simply reflects back into the gas phase, although some long-lived intermediate states (resonances) may exist. The sticking of a diatomic molecule is usually discussed in terms of a ground-state electronically adiabatic potential-energy curve (g.s.e.a.p.e.c.) along the reaction path having an activation barrier separating a weakly bound molecular precursor state (P) from a strongly bound dissociatively chemisorbed state (DC).

Such a potential-energy curve is often thought of as constructed from two *diabatic curves*, one describing the adsorbed molecule, the other the chemisorbed atoms. The diabatic curves are imagined to be constructed in the following way, where for definiteness, we consider the adsorption of N_2.

Wavefunctions $\Phi_0(\mathrm{N}_2)$ for the $^1\Sigma_g$ ground state of N_2, and $\Phi_0(\mathrm{S})$ for the ground state of the solid are antisymmetrized with the operator $\hat{\mathrm{A}}$ to give a wavefunction

$$\Phi_0(\mathrm{N}_2, \mathrm{S}) = \hat{\mathrm{A}}\Phi_0(\mathrm{N}_2)\,\Phi_0(\mathrm{S}), \tag{12}$$

which is then used to calculate the expectation of the exact Hamiltonian at all distances of the molecule from the solid. This is the potential energy curve for the molecular precursor. The other diabatic curve uses the wavefunction $\Phi_0(2\mathrm{N})$ for the $^1\Sigma_g$ state of two nitrogen atoms

$$\Phi_0(2\mathrm{N}, \mathrm{S}) = \hat{\mathrm{A}}\Phi_0(2\mathrm{N})\,\Phi_0(\mathrm{S}). \tag{13}$$

Near the crossing point of the two diabatic curves, where the barrier separating P and DC is located, a better wavefunction than either (12) or (13) separately is their linear combination

$$\Psi = a[\Phi_0(\mathrm{N}_2, \mathrm{S}) + b\Phi_0(2\mathrm{N}, \mathrm{S})], \tag{14}$$

and minimizing the expectation of the exact Hamiltonian with (14) gives an approximate g.s.e.a.p.e.s. for all positions of the two N nuclei in front of the solid.

In a slow collision the N_2 molecule stays on the g.s.e.a.p.e.s. (14); in a fast collision it stays on the diabatic surface defined by (12), and does not get into the chemisorption minimum.

One important point needs to be made in connection with the diabatic curve based on (12). It will not contain the long-range Van der Waals attraction between N_2 and S, and is not therefore suitable for discussing trapping into the precursor.

Returning now to the actual g.s.e.a.p.e.c., an unspecified mechanism for energy exchange between the adsorbate and the substrate is assumed to exist so that the molecule can be trapped in P, and make (slow) transitions out of it, over the activation barrier to DC. The height, E^*, of the barrier determines the rate of chemisorption. If we can lower E^* by increasing the binding energy of P, the rate of chemisorption is increased. Promotors do this; poisons increase E^*. In transition metals, electropositive atoms (Na, K) are promotors in N_2 chemisorption, electronegative atoms (P, S, Cl) are poisons.

These effects are easy to see in the effective-medium theory of chemisorption (Nørskov & Lang 1980; Nørskov 1982; Nørskov *et al.* 1984), where the first-order theory gives the change in the binding energy on the molecule due to the coadsorbed atom as

$$\Delta E_{\mathrm{B}} = \int \mathrm{d}\boldsymbol{r}\, \delta\phi_0(\boldsymbol{r})\, \Delta\rho(\boldsymbol{r}), \tag{15}$$

where $\delta\phi_0(\boldsymbol{r})$ is the coadsorbate-induced electrostatic potential in the substrate, and $\Delta\rho(\boldsymbol{r})$ is the molecule-induced charge density (including the nuclei). Equation (15) is simply the electrostatic interaction between the coadsorbate and the adsorbed molecule.

As an example of recent work that seeks to understand promotors and poisons by using the local density of states (1) evaluated at the Fermi level, namely $\rho(\boldsymbol{r}, \epsilon_F)$, I refer to the work of Feibelman & Hamann (1985). These authors computed $\rho(\boldsymbol{r}, \epsilon_F)$ for thin (i.e. two-layer) films of Rh (100) with, and without $\frac{1}{4}$ monolayer coverages of P, S, Cl, and Li atoms, using the self-consistent l.a.p.w. technique, and a local exchange-correlation potential. Since $\rho(\boldsymbol{r}, \epsilon_F)$ measures the ability of the system to respond at the lowest energy cost to an external perturbation, it is suggested that the larger $\rho(\boldsymbol{r}, \epsilon_F)$ at the adsorbate position, the larger should be the adsorbate binding energy. The computations show that Li increases $\rho(\boldsymbol{r}, \epsilon_F)$ above its clean-surface value at typical molecular adsorbate positions, whereas P, S and Cl lower it. The inference is that Li lowers the activation barrier to chemisorption, while the electronegative atoms raise it. However, there is at present no theory actually relating $\rho(\boldsymbol{r}, \epsilon_F)$ at the adsorbate position to its binding energy.

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