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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
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CHEMICAL BONDS OUTSIDE SOLID SURFACES
(Lecture I)

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1.1 Introduction

We shall be concerned here with the changes induced in a chemical bond when it is brought up from infinite separation to a finite distance from a planar solid surface. The main attention will focus on the chemical bond parallel to the surface, though some discussion will be included of the perpendicular configuration and indeed, the bond at an arbitrary orientation to the surface.

Clearly, the surface might be a whole variety of materials: ionic, covalently bonded networks such as Si or Ge, metallic such at Pt, or semimetallic, e.g. graphite. Furthermore, the results will depend not only on the nature of the surface, whether insulating, semiconducting, or metallic, but on the question as to whether the electron cloud associated with the chemical bond overlaps appreciably with the electron distribution of the solid surface. This serves to give us a gross classification into two regimes:

(a) Physisorption : where there is negligible overlap of electronic charge distributions, and

(b) Chemisorption, where the molecular electrons overlap with the valence or conduction electrons in the planar surface.

It is natural to begin with the physisorption regime and, to be definite, let us consider first a metal surface.

1.2 Physisorption on a planar conducting surface

We shall consider two cases below which, though the same general conclusions emerge from both, require different treatment. The first is when the bond is built from atoms with rather well-defined cores at the equilibrium separation. Then we shall turn to deal with the H_2 molecule; for the present purposes the Heitler–London treatment proves amenable to generalization to account for the proximity of the solid surface.

1.2.1. Bond in molecule with well-defined cores

Let us represent the usual potential energy curve of the homonuclear molecule we shall specifically be concerned with by a Lennard–Jones 6–12 potential. The interaction energy, $\Delta E(R)$ say, between the pair of like atoms at separation R is therefore represented by

$$\Delta E(R) = \frac{B}{R^{12}} - \frac{A}{R^{6}}, \qquad (1.2.1)$$

in free space.

Now consider the effect of the proximity of a metallic conducting surface on $\Delta E(R)$: say when the bond is parallel to the surface. The first term on the RHS of eqn (1.2.1) comes from core repulsion, which can be expected to be insensitive to the proximity of the surface. Thus, attention below will focus on the way the surface influences the magnitude of the dispersion force, characterized by the constant A in (1.2.1).

To see how changes in A affect properties of the bond, let us calculate the equilibrium bond length R_e for which $d\Delta E/dR = 0$. Then it follows almost immediately from eqn (1.2.1) that

$$R_e = \left(\frac{2B}{A}\right)^{\frac{1}{6}} \qquad (1.2.2)$$

which shows, for assumed fixed B, that as A changes from its free space value, R_e is pretty insensitive to modest changes. However, if we now substitute the result (1.2.2) back into eqn (1.2.1) to calculate the well depth, then one readily finds

$$\Delta E\big|_{\min} = -\frac{A^2}{4B}. \qquad (1.2.3)$$

Depending as it does on the square of A, the well depth is plainly quite sensitive to changes in A brought about by the presence of the solid surface.

(a) Calculation of dispersion force in presence of planar conducting surface

The reason why A will be modified when the bond is brought up to the metal surface is readily recognized. Charge fluctuations in the molecule will lead to response of the itinerant electrons in the metal, which will, in turn, induce effects in the molecule.

Following pioneering work by McLachlan(1) the calculation of A in the presence of the conductor was carried out by Mahanty and March (2) using essentially the Lifshitz theory of dispersion forces. Introducing the dimensionless variable.

$$s = \frac{2\ (\text{Distance } z \text{ from surface})}{\text{Diatomic bond length}} \qquad (1.2.4)$$

one can write

$$A = A_{\text{London}} F(s) \qquad (1.2.5)$$

where the free space constant A_{London} may be written

$$A_{\text{London}} = \frac{3}{4} \hbar\, \alpha_1(0)\, \alpha_2(0) \qquad (1.2.6)$$

with $\alpha_j(\omega)$ the polarizability of the jth constituent atom at frequency ω.

Anticipating the result of the argument sketched in Appendix 1.1 for the bond parallel to a perfect planar conductor the function F(s) in eqn (1.2.5) is given explicitly by Mahanty and March (2) as

$$F(s) = 1 + \frac{1}{(1+s^2)^3} - \frac{4}{3}\frac{(1+s^2/4)}{(1+s^2)^{5/2}} \qquad (1.2.7)$$

This function varies monotonically from $\frac{2}{3}$ at $s = 0$ to 1 as $s \to \infty$. Inserting the maximum reduction of A by 2/3 into the equilibrium bond length leads to a small increase of a few %. But clearly, the same assumed reduction factor will make the well shallower than its free space form, according to eqn (1.2.3), by a factor 4/9. Of course, this is the maximum reduction possible with the above simple model.

1.2.2 Application to coverage dependence of desorption energy of Xe on Pt

Evidence in favour of a reduction in the well depth discussed above comes from the work of Redondo et al(3). They used free space interatomic potentials to discuss desorption energy as a function of coverage for Xe on W. Their conclusion was that the desorption energy calculated from these free space potentials varied more strongly as a function of coverage than did that extracted from these potentials.

Subsequently, Joyce et al(4) used the Mahanty–March lateral interaction discussed above, and Figure 1.1 shows the marked reduction in the variation of desorption energy with coverage from the free space potential prediction. This is clearly in the right direction to improve the agreement with experiment. Joyce et al also calculated thermal desorption spectra, to compare with the measurements of Opila and Gomer(5). Quite reasonable agreement with experiment resulted.

The conclusion from this work is that the data supports the theory of lateral interactions outside a metal surface in the physisorption regime.

We note here that Mahanty and March(2) also considered the perpendicular configuration. The function F in eqn (1.2.5) is now an enhancement factor, with a maximum value of 8/3 and minimum value unity. But now, unlike the parallel configuration, interaction of individual atoms with the surface is very different and must be included. One anticipates in this perpendicular configuration that the bond length will be reduced, while the bond strength will be more dependent on detail for this orientation than for the parallel case. Finally, Mahanty and March considered a bond at arbitrary orientation; this work has been extended subsequently by Mahanty et al(6) to whose paper the interested reader is referred for full details. A brief sketch of the method and results has been included at the end of Appendix 1.1 here.

1.2.3 Case of H_2 molecule: modification of Heitler–London theory to include image effects

As already mentioned, the previous argument is only useful when cores are well defined at the equilibrium separation. The interesting case of the H_2 molecule therefore requires separate treatment. This was given by Flores et al(7), their argument resting on two assumptions:

(i) The Heitler–London theory affords a useful starting point, for a semi–quantitative study

(ii) The Coulombic interaction $|/|\, r_a - r_b|$ between two charges a and b is to be replaced, in the presence of a conducting surface, by

$$\frac{1}{|r_a - r_b|} - \frac{1}{|r_a - r_b^{I}|},$$

I referring to an image distance.

The approach subsequently follows closely the traditional Heitler–London calculation. Thus the molecular energy E is written as

$$E = 2E_{1s} + \frac{J}{(1 + S^2)} + \frac{K}{(1 + S^2)}, \qquad (1.2.8.)$$

and one then must examine the behaviour of the Coulomb piece J and the exchange term K in the presence of the metal surface, S being the overlap integral between hydrogen 1s wave functions.

Calculation shows J to play an unimportant role and the correction to the Heitler–London energy due to the metal surface may be written

$$\delta E = \delta K/(1 + S^2). \qquad (1.2.9)$$

With the interaction between charges modified by the image term as in assumption (ii) above, δK was calculated (see Appendix 1.2) by Flores et al(7). Again, in the parallel configuration, the bond is weakened and (slightly) lengthened.

1.2.4 Insulating and semiconducting surfaces, as well as metals

More briefly, we shall now comment on lateral interactions in the physisorption regime for some insulating and semiconducting surfaces in addition to metals, full details being relegated to Appendix 1.3. The account follows that given by Girard and Girardet(8) fairly closely.

There has been considerable effort aimed at identifying all the contributions of the interaction of adatoms with both dielectric and metallic substrates according according to the adsorbate coverage rate. Bruch has discussed the various dominant terms in the lateral interaction and has analyzed the dominance of the substrate–mediated energy for rare gas monolayers adsorbed on noble metals (cf section 1.2.2) or on the semi–metal graphite.

As Girard and Girardet(8) emphasize a fully quantitative determination of the latter energy per adatom requires the calculation of (a) the corrugation energy of the surface, of (b) all the substrate–mediated energies including the long–range dispersion contribution discussed in Appendix 1.3, the long– and short–range electrostatic terms and the elastic distortion of the surface, of (c) the proper energy of the adatom in the monolayer including many–body effects and (d) the influence of finite temperature.

Hence, it is difficult to discuss the relative importance of the long–range substrate–mediated contribution if the monolayer configuration is not known. One can however assert that the corrugation decreases when the metal face becomes more dense and, in contrast, that the substrate–mediated

long–range energy increases with the atomic density of the face and with the size of the adatom. This fact necessitates an accurate determination of the substrate–mediated term for graphite and noble or transition metals with the more dense (0001) and (111) faces, respectively. Indeed, it appears that this term, in this case, is dominant in determining the structure of the adsorbed monolayer.

For molecules adsorbed in ionic surfaces, the substrate–mediated dispersion energy remains weak when compared with the multipolar induction terms. These terms fundamentally depend on the relative orientations of the adsorbed molecules and on the orientation of the molecules in their adsorption sites. For ionic crystals, the corrugation energy is generally greater than for metals and the study of the relative magnitude of the contributions to the lateral energy is required to determine the monolayer structure.

A remark should be added on other interaction mechanisms which can be classified in the substrate–mediated energy (see, for example, Bruch(9)). For instance, the interaction between dipole moments induced by the proximity of the metal in the case of rare gas atoms have been disregarded. In a similar way, the quadrupole and higher multipole moments would modify the form and the magnitude of the multipolar induction energy between adsorbed molecules.

1.3 Chemisorption of metallic surfaces

Having discussed especially lateral interactions in the physisorption range at some length, we must turn now to the case when the metal–chemical bond interaction is strong, due to appreciable overlap of the molecular electron distribution with the itinerant electrons in the metal.

Then the question immediately arises: how does a 'perturbation' embedded in an electron gas affect the metal electron distribution. We shall see below that the answer to this question has an important bearing on the nature of the lateral interactions between atomic or molecular species outside a conducting surface in the chemisorption regime.

1.3.1 Elementary metal models

Let us start from electrons in a one–dimensional box of length ℓ, with origin $z = 0$ at one edge of this box. Evidently the electron density $\rho(z)$ for N singly filled levels is given by the sum of the squares of the normalized wave functions:

$$\rho(z) = \frac{2}{\ell} \sum_{n=1}^{N} \sin^2 \frac{n\pi z}{\ell} \qquad (1.3.1)$$

This can be summed exactly to yield, with $y = \frac{\pi z}{\ell}$:

$$\rho(z) = \frac{N + \frac{1}{2}}{\ell} - \frac{1}{2\ell} \frac{\sin(2N + 1)y}{\sin y} . \qquad (1.3.2)$$

We shall be interested in the 'perturbation' induced by the edge of the box at $z = 0$ deep in the Fermi gas : this we can obtain by taking the limit when the length of the box ℓ tends to infinity. One can either take this limit, such that $N/\ell \to \rho_0$, the constant 'bulk' density, in eqn (1.3.2), or quite equivalently one can return to eqn (1.3.1) and replace the summation by an integration. Either way, one readily obtains the desired result

$$\rho(z) = \rho_0 \left[1 - \frac{\sin\ 2k_f\ z}{2k_f\ z} \right] \qquad (1.3.3)$$

where we have introduced, via the usual phase space argument, the Fermi wave number k_f, related to ρ_0 for singly filled levels by $k_f = \pi\rho_0$.

Two points are to be noted from the elementary model result (1.3.3):

(i) The electron density ρ rises from zero at $z = 0$, the position of the infinite barrier, to its aspymptotic bulk value ρ_0, oscillating about its asymptote with wavelength π/k_f : ie the long–range oscillations are determined by the de Broglie wavelength of an electron at the Fermi surface.

(ii) The density ρ first reaches its bulk value ρ_0 after a distance given by $2k_f\ z = \pi$, and so one can say that the 'thickness' of the surface 'spill–out' of the electron density distribution in a simple metal is also $\sim \pi/k_f$ which is ~ 1Å.

In a semi–infinite three–dimensional electron gas with an infinite barrier, eqn (1.3.3) is replaced by the result

$$\rho(z) = \rho_0 \left[\frac{1 - j_1(2k_f z)}{2k_f z} \right], \qquad (1.3.4)$$

which was first obtained by Bardeen(10). His model is considered in more detail; following the work of Moore and March(11), in Appendix 1.2.

1.3.2 Relation of long–range oscillations in perturbed electron density to lateral interactions between chemisorbed species

Of course, we want to relate what has been learnt about long–range oscillations induced by perturbations in a Fermi gas of itinerant metal electrons to the (indirect) lateral interactions between chemisorbed species outside a planar metal surface. The detailed argument is given in Appendix 1.2, but we note here that for a weak perturbing potential $V(r)$ the charge $\rho(r) - \rho_0$ displaced by the perturbation follows from linear response theory as

$$\Delta\rho \equiv \rho(r) - \rho_0 = \int F(r\,r')\,V(r')\,dr' \qquad (1.3.5)$$

The kernel F must be calculated for the appropriate situation. For a perturbation in a bulk electron gas, F was obtained by March and Murray$^{(12)}$ as

$$F(t) = \frac{j_1(2k_f t)}{(2k_f t)^2} \qquad (1.3.6)$$

with $t \equiv |r - r'|$.

If $V(r') = \lambda\delta(r')$, it follows immediately from eqn (1.3.5) that

$$\Delta\rho(r) \sim \frac{j_1(2k_f r)}{r^2} : j_1(x) = \frac{\sin x - x\cos x}{x^2} \qquad (1.3.7)$$

or at sufficiently large r,

$$\Delta\rho(r) \sim \frac{\text{constant} \cos(2k_f r)}{r^3} \qquad (1.3.8)$$

This form is to be compared with the forms (1.3.4) or (1.3.3.) : all exhibit long–range oscillations, but one must be careful about the inverse powers of distance : this is the essential point we shall stress below. Actually, for a test charge perturbation, eqn (1.3.5) can be combined with Poisson's equation and leads to a self–consistent field problem. When solved, precisely the form (1.3.8) is regained, with the same oscillatory decay with distance for the screened potential round the test charge. The so–called electrostatic model then leads to the interaction energy between test charges at separation R as

$$\Delta E(R) \sim \frac{A \cos 2k_f R}{R^3} \qquad (1.3.9)$$

As Corless and March$^{(13)}$ demonstrated, eqn (1.3.9) is valid for charges interacting in a bulk metal. Near a surface, one can use the Bardeen model developed in Appendix 1.2 to re–calculate the function F in eqn (1.3.5). Then, for a pair of charges parallel to the surface, the argument of Appendix 1.2 reveals a shorter–range oscillatory interaction, still valid asymptotically, having the form

$$\Delta E(R)\Big|^{\text{linear response}}_{\text{chemisorption}} \sim \frac{A \cos 2k_f R}{R^5} \qquad (1.3.10)$$

Following pioneering work by Grimley, and by Eistein and Schrieffer, the linear response form (1.3.10) was derived independently by Flores et al$^{(7)}$and by Lau and Kohn$^{(14)}$.

Just as Friedel and co–workers showed for the bulk metal result (1.3.9), when the 'pertubation' scatters the itinerant electrons strongly there is a phase shift ϕ introduced into the asymptotic form (1.3.10) to yield for the indirect lateral interaction

$$\Delta E(R)\Big|_{\text{chemisorption}} \sim \frac{A \cos(2k_f R + \phi)}{R^5} \qquad (1.3.11)$$

Below, we shall mention two applications of the indirect long–range oscillatory interaction between chemisorbed species: the first for H on Pt and the second for CO molecules interacting also outside a Pt surface.