Theory of Electrical Double Layers in Adsorbed Films

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The nature of an absorbed layer is discussed in terms of quantum mechanics, and the factors governing the sign and magnitude of the electrical double-layer are determined. Although the ionization potentials of Ca, Sr and Ba are greater than the electronic work function of tungsten, a sparse distribution of these atoms on a tungsten surface behaves in a way quite similar to atoms of alkali metals whose ionization potentials are much smaller. This behavior can be understood only in terms of quantum mechanics.

§1.

T is well recognized that quite a sparse dis-L tribution of foreign atoms adsorbed onto a metal surface suffices to give rise to a strong electrical double-layer, which may be positive outwards or negative outwards according to the nature of the adsorbed atoms. That atoms of the alkali metals K, Rb and Cs, should reduce the effective work function of tungsten in this way has always been regarded as in agreement with expectation. Their ionization potentials (4.3, 4.1 and 3.85 e.v.) are smaller than the work function of tungsten (about 4.5 e.v.), and consequently, it is said, they will give up their valence electron to the metal, and the positive cores lying on the surface will give rise to an electrical double layer positive outwards.

To invoke the fact that the ionization potential is less than the work function of the underlying crystal is, however, to set up an unsatisfactory criterion. For it is found that a sparse distribution of barium atoms behaves very like caesium. The work on calcium and strontium has not been published; but Dr. Becker has kindly written to me that the curves for these metals are similar to those of barium, i.e., they reduce the work function of tungsten, though to a smaller extent. Yet the first ionization potentials of these elements—6.09, 5.67 and 5.2 e.v.—are all greater than the work function of tungsten. According to the simple picture they should not give up their electrons to the metal.

§2.

In order to see whether the work function is raised or lowered, we wish to know the electron density at the surface of a metal A near a point where an atom of a foreign metal B is adsorbed. This information will be most easily obtained by first considering in detail the state of affairs when the atom B, or its core, is held at a distance of a few atomic diameters from the surface; later we shall consider what happens when this distance d from the surface is diminished. We need to know the potential energy of an electron along a line perpendicular to the surface of A and passing through the core of B. Curve a of Fig. 1 shows this potential energy, using the Bloch model for the metal, and curve b using the simpler Sommerfeld model. In curve c the "potential box" provided by the core has been replaced by a rectangular potential box, which is useful for a preliminary treatment. For the sake of brevity, we shall proceed immediately to discuss this energy diagram by the methods which have recently been described in extenso by the author.¹ In the first place, if the box RSis deeper than PQ, and possesses an allowed level lying below the bottom of the box PQ, this level will remain discrete when the distance QRis diminished. Atoms with low-lying levels of this type will be discussed later. But each of the elements mentioned above has a valence level which will lie near the critical level of the metal: let the energy of this valence level be W_a . If we insert the potential energy of Fig. 1 into the Schrödinger equation, and solve, we obtain a set of allowed levels which belong jointly to the metal and to the atom. Strictly speaking, the atom has as many allowed levels as the metal, namely, millions. Yet when an atom is not too near to the surface we usually regard it as having a valence level, which may be somewhat broadened by the presence of the neighboring solid;

¹Gurney, *Elementary Quantum Mechanics*, Cambridge University Press, 1934.



FIG. 1. Potential energy curves for an electron at the surface of a metal along a line passing through the core of an atom; curve a, for a Bloch model, curve b, for a Sommerfeld model, curve c, for a simplified rectangular potential box picture.

and we are certainly right in doing so. It will be convenient to state here exactly what we mean by this conception. We mean that the solutions of the Schrödinger equation are such that for certain values of W on either side of W_a the amplitude which the wave function has around the atomic core is large compared with the amplitude which it has inside the metal, while for all allowed energies more distant from W_a their amplitude around the atomic core is smaller than in the metal by a factor e^{-kd} , where d is the distance from the metal surface, and k depends on the height of the potential barrier. When d is large, the factor e^{-kd} is so small that we may regard the atom as having an almost sharp level of value W_a . The blurred level has no sharp edges, and if the atomic core is brought nearer to the metal, the level becomes broadened, owing to the increase in the value of e^{-kd} . In Fig. 2 let ordinates be W, and let abcissae be the mean value of $|\psi|^2$ around the atomic core when the latter is at a particular distance from the metal. Curve a shows the level when still fairly narrow, and curve b a broader band when the atomic core is nearer to the surface. When finally the atom is deposited on the surface, and the value of d is only one or two Angstroms, it is easily calculated² that the value of e^{-kd} is as large as 10^{-1} or more. Hence there are no longer near W_a any values of W for which the amplitude of ψ around the atomic core is much smaller or much larger than in the interior of the metal.

Returning to curve a of Fig. 1, we recall that the free electrons in a metal move about freely



FIG. 2. Broadening of an energy level as the adsorbed atom approaches the metal surface.

FIG. 3. Representation of the filling of an atomic band up to the Fermi level; a, for an element of low ionization potential, b, for an element of rather higher ionization potential.

because the potential barriers between adjacent cores are transparent to the electrons. And we see now that, when the metallic atom B is adsorbed, the potential barrier between its core and the adjacent cores of the lattice is likewise transparent to the free electrons of the underlving metal. In its interior this underlying metal is neutral in every part, not because a valence electron is resident in every atom, but because the moving electrons spend on the average as much time in each atom as is required to produce uniform neutrality. In the same way, when the atom B is adsorbed, there will not be an electron resident in the atom, nor will there be a vacant level. But in every second 10^{14} or 10^{15} free electrons will approach this point of the boundary from within, and these will neutralize the positive core of B to a certain extent which we must now discuss.

The whole argument so far has dealt with the normalized wave functions appropriate to the potential energy of Fig. 1, without regard to the question as to whether they were occupied by electrons or not. When an atom of an element A is deposited on a crystal of A at ordinary low temperature, it is of course the critical Fermi level of the metal which determines which levels will be occupied, and which vacant. And we come now to the most important factor in the problem, namely, that when an atom of B is adsorbed onto a metal A, it is still the Fermi level of A which determines the extent to which the positive core of B is neutralized by valence electrons. The state of affairs may be visualized as in Figs. 3a and b. These represent the atomic

² Reference 1, Chapter 3.

band filled with electrons up to a certain level (the Fermi level) (a) for an element B of low ionization potential, and (b) for an element of rather higher ionization potential.

§3.

We have been dealing hitherto with the adsorption of atoms of any element B which has an ionization potential comparable with the work function of the metal A. There are, however, elements whose characteristic valence levels lie much lower, for example, oxygen with ionization potential 13.6 e.v., much greater than the work function of any metal. The adsorption of such an atom is somewhat different, because any level which falls below the valence band of the underlying metal will remain a single discrete level. It will be a localized level, with the amplitude of ψ falling off exponentially within the metal. It behaves like one of the x-ray levels which we have been able to disregard.

It is a property of elements like oxygen, that an atom in vacuum is able to accommodate a supernumerary electron and to become a negative ion. The potential energy which an additional electron has in the field of the neutral atom is such as to give a stable quantized state with the electron bound. When the atom is isolated, this vacant level is sharply defined; if the atom is brought towards a metal surface the level will become broadened out into a band, exactly as in the case of a valence level. It will again be the critical level of the underlying metal which determines to what extent this band is invaded by electrons from the metal. This will give rise to a double layer negative outwards, since we have an already neutral atom playing the part which was formerly played by a positive core. It is found that the adsorption of oxygen raises the work function of tungsten from 4.5 to more than 8 e.v.

Only positive double layers have been studied in detail experimentally; we will accordingly develop the discussion of Fig. 2. If the band of the adsorbed atom lies mainly above the Fermi level of the metal, as in Fig. 3a, the positive core will be only slightly neutralized by the electron cloud. If the center of the band lies near the Fermi level, the band will be about half full. One must not, however, conclude that the positive core is necessarily neutralized to a greater extent in the second case. For the valency of the adsorbed atom is also a determining factor. To neutralize the positive core of a monovalent atom it is only necessary that half the band be filled.3 For a divalent atom, on the other hand, the whole band must be filled. If therefore the band of Fig. 3a is that of an adsorbed alkali atom, and that of Fig. 3b of a divalent atom, the contribution to the electrical double layer would be about the same, in spite of the fact that $I < \phi$ for the former, and $I > \phi$ for the latter. The remarkable similarity in the behavior of the alkalis and the alkaline earth metals on tungsten is thus to be expected.

§4.

In discussing the relation of the atomic band of B to the critical level of A, we have hitherto spoken as if for any two elements A and Bthere is a unique relation. There exists a unique relation so long as the number of adsorbed atoms is small. But it is found, for example, that when a tungsten surface is only one-tenth covered with caesium atoms, the electronic work function is already reduced by 0.8 e.v. This drop of potential takes place at the metal surface, as may easily be established by drawing the equipotential lines which run parallel to the surface between the adsorbed charges and their electrical images in the metal. The potential energy curve of Fig. 1 is of course modified, and the wave function for any energy W is no longer the same as before. In a positive layer the atomic band is shifted downward relative to the critical level of the metal, and consequently is invaded to a greater extent by electrons from the metal. When many atoms are present each atom makes a smaller contribution to the double layer than when few are present. When fresh atoms are deposited, each atom makes a positive contribution to the layer, but the growth of the potential drop diminishes the contribution being made by every atom already present. The strength of the double laver therefore does not grow linearly with the number of atoms deposited.⁴ Clearly we may

³ Gurney, reference 1, Chapter 8.

⁴ Becker, Trans. Faraday Soc. 28, 151 (1932); Taylor and Langmuir, Phys. Rev. 44, 437 (1933).

even come to a stage in which the positive contribution by the added atom is almost wholly counterbalanced by the small diminution which it automatically causes in the contributions of the very large number of atoms already present in the film. It is, in fact, found that in the case of both caesium and barium the strength of the double layer passes through a maximum value.

An isolated atomic particle in vacuum must be exactly electrically neutral, or else must bear a charge $\pm ne$ where *n* is an integer. This is not true of an atom forming part of a polar molecule. And the essential basis of the above discussion is that there is no reason why this should be true of atoms adsorbed onto a metal surface. Recent experimental work has, however, been interpreted in terms of the separate existence of ions and neutral atoms on the surface. When the author criticized this interpretation at a meeting of the Faraday Society, Dr. Becker in his published reply wrote,

The chief reason for believing that some adsorbed particles are completely ionized is the experimental fact that when caesium is evaporated from a hot tungsten surface sparsely covered with caesium, practically every particle comes off as an ion. Now, if the forces on the caesium adsorbed on the tungsten surface are not sufficient to completely ionize some of the caesium, one would not expect these forces to be sufficient to ionize the caesium when it is further from the surface and escaping from it. Consequently no caesium should evaporate as ions unless it is adsorbed on the surface as an ion.

More recent work has been interpreted in the same way.⁵

To clear up this question one must consider what happens when any metal atom tries to

escape from the surface. The process pictured in Fig. 2 takes place in the reverse direction; the broad band of levels closes up into a narrow band, and tends to the discrete characteristic valency level of the atom in vacuum. This level may be above or below the Fermi critical level of the metal, depending on the ionization potential of the element considered and the effective work function of the metal modified by any double layer there may be present. Whether the particle escapes as an ion or a neutral atom depends entirely on what level in the metal happens at the moment to be opposite to the characteristic level of the atom. The motion of electrons being some thousand times more rapid than the thermal velocity of an ion, there is plenty of time for an electron to pass through the potential barrier of Fig. 1a while the atomic core is in the act of leaving the surface. In the case of caesium (ionization potential 3.85 e.v.) on sparsely covered tungsten (effective work function more than 4 e.v.) the characteristic level finds itself opposite an almost unoccupied level in the metal. The electron is accordingly almost always left behind in the metal. For progressively thicker films of caesium, the valency level of the escaping caesium becomes progressively lowered towards and beyond the Fermi critical level of the metal. We should therefore expect the proportion of caesium escaping as ions to be diminished, the fraction following exactly the Fermi population of the metallic levels at the temperature of the experiment. A double-layer of strength 0.7 volt should suffice to make the number of atoms and ions escaping of the same order of magnitude, since the work function of pure tungsten is about 4.5 volts; this is found to be the case.

⁶ Evans, Proc. Roy. Soc. A145, 135 (1934); Proc. Camb. Phil. Soc. 29, 161 (1933).