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To cite this version:

HAL Id: jpa-00229901
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Submitted on 1 Jan 1989

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ON DIFFERENT TYPES OF DIPOLE-DIPOLE INTERACTION

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Abstract - This paper offers comments on some recent theoretical work, and more generally on the origin of field adsorption. It is suggested that neglect of atomic structure in recent calculations has led to invalid conclusions, and that some criticisms of the array model are misplaced. The results of an approximate classical model for field enhancement above a protruding atom are presented, as part of a comparison between theory and experiment. It is suggested that the neon "hopping bright spot" phenomenon could be a better flag bearer for exchange-integral effects, provided that cluster calculations can predict the apex location of adsorption. Possibly both exchange-integral and polarisation terms contribute to observed effects.

1. Introduction

This paper has two aims. First, to comment on the paper by Kreuzer /1/ at last year's Field Emission Symposium, and on a related paper by Watanabe, Payne and Kreuzer /2/, and to reply to their criticisms of the Forbes and Wafi "array model" /3/. Second, to make some general comments about the origin of field adsorption, and the extent to which the relative importances of exchange integral induced effects and polarisation effects have been demonstrated. A fuller version of these comments will be presented elsewhere (Surface Science, to be published), so in some places only results and an outline of the arguments will be presented. It is necessary to deal first with some background issues.

1.1 Field-induced dipole-dipole interactions

Confusion has arisen in the past because the phrase "field-induced dipole-dipole interaction" has been used as a name for two different physical interactions. Both are types of physisorption interaction, and I call them the image-related dipole-dipole interaction and the structure-related dipole-dipole interaction.

The image-related dipole-dipole interaction is seen most clearly in theories that neglect atomic structure and postulate a perfectly smooth model surface, with a uniform field above it. In the field an atom develops a dipole moment, and this dipole moment interacts with its image in the surface. (There will also be a small enhancement of the adatom dipole moment.) In the absence of the external atom the surface charge distribution is LATERALLY UNIFORM.

The structure-related dipole-dipole interaction can only occur in models that take surface atomic structure into account. It is hypothesised that the applied voltage induces a surface charge distribution that (in the vicinity of a protruding surface atom) has something of the character of an electric dipole. The structure-related dipole-dipole interaction is the interaction between this field-induced surface dipole and the field-induced dipole in the external atom. Note that this surface dipole represents a LATERAL NON-UNIFORMITY in the surface charge distribution that is PRESENT in the absence of the external atom.

1.2 Classical calculation of the image-related dipole-dipole interaction

In the International System of Measurement, the classical interaction between a dipole of moment \( p \) and its image in a smooth surface, in lowest order, is (e.g. Ref./4/, p.55):

\[
\Delta U(1) = -\frac{1}{8} \frac{p^2}{4\pi\varepsilon_0 s^3}
\]

where \( \varepsilon_0 \) is the electric constant, and \( s \) is the distance of the dipole centre from the image plane. Eq.(1) is derived by considering two pairs of opposite charges, each pair having a small fixed separation, summing the four image interactions, and taking the lowest term.
The classical calculation presumes that the separation of the charges does not change as the dipole approaches the surface, and thus applies directly to the case of a permanent dipole. With a field-induced dipole, let the uniform "external" field above the surface be $\mathbf{F}$ and the dipole polarisability be $\alpha$. Distant from the surface the moment is $aF$; on approaching the surface there will be a small increase in moment, due to the field of the image dipole. The classical interaction energy can be split into two terms. The first represents the work done in bringing up a dipole of constant moment $aF$ to the bonding equilibrium position, and is:

$$\Delta U(1) = -\frac{1}{8} \frac{\alpha^2 \mathbf{F}^2 \alpha \sin \theta}{\sigma^3}$$

For helium, taking $\mathbf{F}$ as 56 V/nm and $s$ as 170 pm gives $\Delta U(1)$ as $-2.3$ meV.

The second term is a correction representing the energy changes associated with relaxation (at the equilibrium position) of the dipole from moment $aF$ to moment $\alpha F_{\text{loc}}$, where $\alpha F_{\text{loc}}$ is the local field (including image dipole effects) at the equilibrium position. Details of this calculation will be presented elsewhere. The results are that $\alpha F_{\text{loc}}/F = 1.011$, and the correction (using the above parameter values) is $-0.07$ meV. Thus expression (2) provides a good classical estimate of the interaction energy for a field-induced dipole.

1.3 The Forbes and Wafi Array model

This is intended to model the field and potential distributions above an atomically flat (but not close-packed) positively charged surface. It has three components: (i) an array of positive charges situated at the positions of the surface atom nuclei, each charge being of a size necessary to satisfy the Gauss result; (ii) an array of polarisable dipoles, also situated at the positions of the surface nuclei, with a polarisability value chosen to make sure that the electrical reference surface is in the place found experimentally; (iii) a distant array of negative charge, that gives rise to a uniform field $1/2F$ at the surface, necessary for electrostatic self-consistency.

The rationale behind this model as follows. For regions of space outside the surface electronic wave-functions, the time-average field and potential distributions associated with the surface sources can be calculated by substituting the corresponding classical charge distributions. Then the effects of a distributed charge distribution can be approximated by representing it by point charges and multipoles of appropriate strengths, via the multipole approximation of classical electrostatics.

There are a number of reasons for choosing a localised model for the charge distribution, including: (a) the fact that atoms are visible in the PIM; (b) possible comparability with the theory of dielectrics, as far as the top layer of atoms are concerned; (c) the probability that some ion-core polarisation is involved. Nevertheless, the array model is an approximation of uncertain validity. We continue to need good, self-consistent, quantum-mechanical calculations; the work of Inglesfield /6/ shows some promise.

2. Discussion of References /1/ and /2/

The work in references /1/ and /2/ aims to show that dispersion and polarisation forces are not strong enough to bind rare gases on field-ion tips. Their method is to carry out a calculation of the image-related dipole-dipole interaction. This paper comments first on the validity of their calculation, then on the scientific status of their conclusions, and then on statements made concerning the array model. Their arguments are given more fully in Ref./2/, and I refer mainly to this paper, here called "WPK".

2.1 Self-consistency of the WPK Hamiltonian

Refs. /1/ and /2/ write the system Hamiltonian $H$ in the form:

$$H = H_s + H_a + H_{sa}$$

The unperturbed Hamiltonian is taken to be the sum of: (1) the Hamiltonian $H_s$ for a potential adatom when in field-free space; and (2) the Hamiltonian $H_a$ for a charged solid filling a half-space and with an appropriate surface electronic charge distribution. WPK then take the perturbation to be the interaction $H_{sa}$ between the solid and the external atom, which they write in the (unrationalised) form:

$$H_{sa} = \int dx \int dx \frac{\rho_s(x) \rho_a(x)}{|x-x|}$$
where $\vec{p}^S$ and $\vec{p}^A$ are operators relating to charge densities $\rho^S$ and $\rho^A$ associated with the solid and the external atom, respectively, and $r$ and $x$ represent coordinate sets associated with the solid and the atom respectively.

However, this model of a charged solid filling half of space contains an infinite amount of charge; therefore it is electrostatically inconsistent. An electrostatically consistent physical model must contain the charge missing from the Ref. 1/2/ model. This can be done by including a "negative plate" parallel to the solid surface and a large distance from it, and placing on this plate a charge of the same surface density as the excess charge on the solid but of opposite sign. The system Hamiltonian must then be written:

$$H = H_S + H_A + H_{FA} = H_S + H_A + H_{SA} + H_{na}$$  \hspace{1cm} (5)

where $H_{FA}$ represents the interaction between the charges in the external atom and all sources of the field, and $H_{na}$ the interaction between the atomic charges and those on the negative plate. $H_{FA}$ can be written formally as:

$$H_{FA} = \int dx \, \vec{p}^A(x) \left[ \int dr \, \vec{p}^S(r) / |r-x| + \int dx_0 \, \vec{p}^A(x_0) / |x_0-x| \right]$$  \hspace{1cm} (6)

where $\vec{p}^A(x_0)$ is the operator associated with the charges on the negative plate, and $x_0$ is the corresponding set of coordinates.

The insufficiency of the perturbation expression (4) can also be demonstrated explicitly. The operator (4) is based on a classical expression of the form:

$$H_{SA \text{ (classical)}} = \int dx \, \rho^S(x) \, \phi^S$$  \hspace{1cm} (7)

where $\phi^S$ is the electrostatic potential due to the charged solid $s$. Well above the surface, the field derived from $\phi^S$ will be normal to the surface. Let this field be $F^S$, and let $z$ be the coordinate normal to the surface. $F^S$ is given by $-\phi^S/\partial z$, so we have:

$$F^S = -\frac{\phi^S}{\partial z} = -\frac{\partial}{\partial z} \int dr \, \rho^S(x) / |r-x|$$  \hspace{1cm} (8)

For calculating $F^S$, it is a sufficient approximation to replace the solid charge distribution $\rho^S$ by a uniform surface charge distribution of density $\sigma$ equally to $F/4\pi$ (i.e. the Gauss result in unrationised units), and carry out a surface integration. The result is $1/2F$.

That is, the field $F^S$ derived from the classical potential term $\phi^S$ (that forms the basis of the perturbation Hamiltonian $H_{SA}$) is not equal to the known field $F$ above the surface. Therefore the expression $H_{SA}$ does not correctly represent the interaction between the atomic charges and the real field $F$ above the charged solid $s$. Without going through the WPK theory in detail, it is difficult to predict what will be the exact effect of including the $H_{na}$ term. However, a first guess is that it may be necessary to replace $F$ by $(2F)$ in some or all of any expressions involving the symbol $F$ that are derived from the WPK theory.

Let us now look at the WPK result for the image-related field-induced dipole-dipole interaction energy. They obtain an expression /2/ that in our notation becomes:

$$\Delta U(1) = -\frac{1}{32} 4\pi^2 \frac{\alpha^2 \nu^2 s^4}{4\pi \delta s^3}$$  \hspace{1cm} (9)

where $s_\nu$ is a slightly complicated distance term. It is seen that their result contains a factor $1/32$ rather than the factor $1/8$ that appears in the classical result. WPK comment on this discrepancy: their view is that the factor $1/8$ obtained from classical theory is applicable only to the case of a permanent dipole interacting with its image; they state that for a field-induced dipole a further factor of $1/4$ pertains.

However, classically, there is no difference between the works done by image forces on (a) a permanent dipole and (b) an induced dipole that drifts up to a surface without any significant change in its dipole moment. There seems no good reason why these works should be different in a quantum-mechanical argument. It seems more likely that the discrepancy (a factor of 4 is exactly what would be expected) is due to use of an incorrect Hamiltonian.

Error by a factor of 4 does not matter much in the present context, since all involved are agreed that the absolute size of the image-related dipole-dipole interaction is small. However, it would (for example) be important to use a correct system Hamiltonian in a fully self-consistent theory of field-induced chemisorption.
2.2 On the status of the WPK conclusions

On p.525, WPK say that their paper will "set up a rigorous theory of polarisation and dispersion forces between polarisable atoms and solids in the presence of high electric fields", and that their "main conclusions will be that (i) neither forces are strong enough to explain field adsorption and (ii) that there is no basis for either the IDP model or the array model". (The "IDP" model is Tsong and Müller's "Isolated Dipole Pair" model /7/.)

In the present author's view, it is potentially misleading for the WPK theory to be described as rigorous. First, there is the difficulty with the system Hamiltonian, already discussed. More important, in the development of the WPK theory there is no mathematical implementation of the fact that real surfaces have an atomic structure. In the context of field-ion microscopy, it seems inappropriate to describe as "rigorous" any theoretical model that disregards the existence of surface atomic structure.

The point is that, if structure-related dipole-dipole interactions really do exist, then it is highly likely that (except, perhaps, on close-packed surfaces) they will result in significantly greater binding energies than do image-related dipole-dipole interactions. But structure-related surface dipoles and their effects can occur only in theoretical contexts that allow for the presence of atomic structure. There is no surface atomic structure in the WPK theory, so it is LOGICALLY IMPOSSIBLE for valid conclusions to be drawn from it about the role of structure-related dipole-dipole interactions, or about the size of polarisation induced effects, or about whether polarisation-induced effects are strong enough to explain field adsorption. The WPK theory can also say nothing about the validity of the IDP and array models, which are models for the charge distribution at an atomically structured surface.

2.3 Response to criticisms of the array model

At this point, it is useful to distinguish three issues: (1) whether field adsorption is predominantly due to exchange-integral effects; (2) whether the charge distribution at a real structured surface has a nature that is characterised by some degree of lateral localisation of excess charge and dipole moment; and (3) whether the IDP and/or array models are likely to provide good representation of such a structured charge distribution, if it exists. As will be seen later, it seems that exchange-integral effects are important, but so are local field and potential variations. The need for surface charge models therefore still exists, and the usefulness of the array model is a cogent question.

In ref./2/, WPK make a number of statements concerning the array model. A reply to these follows. There is, of course, some danger in taking statements out of their contexts; readers are invited to refer to Ref./2/ for the full context of the quotations below.

2.3.1

On p.523, WPK write "To understand the shortcomings of these two models it is useful to recapitulate a few facts about electric fields at surfaces". They then go on to comment that "applying an external electric field" has two effects: the induction of a net charge in the surface, and a modification of the surface dipole layer; and they further comment that these features have been elegantly demonstrated by Gies and Gerhards /9/ and by Schreier and Rebentrost /9/ in the context of jellium calculations.

This last remark is true, but the full history of the surface dipole layer concept does not emerge clearly. The idea of individual surface dipoles was first introduced by Tsong and Müller /7/, but the field adsorption evidence cannot, particularly now, be held to prove that surface dipoles exist. The need from experiment for there to be an induced surface dipole layer at a charged surface emerged much more definitively from the anomalous appearance energy measurements of Culbertson et al. /5/, and their interpretation by Forbes /10/. The existence of the induced surface dipole moment has been implicit in past work based on jellium models of charged surfaces, but it is only recently that results have been explicitly interpreted in this way.

Thus we now have the situation that both the classical array model and the jellium model are in agreement that this surface dipole layer exists, though they disagree as to the extent that the surface dipole layer is localised laterally. There is also agreement that the effect of the surface dipole layer is to induce field repulsion.

No major shortcoming in the array model emerges from WPK's comments. However, the work of Refs. /8/ and /9/ does show more clearly than ever that the concept of "field penetration" into (jellium models of) metals, widely employed in past field-ion literature, is spurious.
On the top of p.531, WPK write: "It should by now be obvious where the IDP and array models go wrong. They assume: (i) that the field penetrates fully into the metal beyond the topmost layer of ion cores...."

This criticism is valid for the IDP model. However, for the array model the remark is mistaken; probably WPK have not taken into account the distant negative charge in the array model. On the metal side of the surface nuclei, the fields due to the layer of positive charges and to the distant negative charges tend to cancel, and although there is obviously some penetration this dies off with a characteristic distance of about a surface-lattice spacing.

There is also a sense in which this criticism is largely irrelevant. In the array model, no attempt is being made to model field distributions inside the metal surface. Rather, the objective is to model the (time-average) field and potential distributions outside the surface wave-functions, by replacing these wave-functions with the corresponding classical charge distribution and using the multipole approximation of classical electrostatic theory.

A further criticism made by WPK at the top of p.531 is that the IDP and array models "assume that this full electric field is further enhanced by the field generated by the induced dipole layer" (which they do). The WPK view is that "this is not justifiable as the induced changes in the dipole layer are part and parcel of the charge redistribution in the metal surface that leads to the expulsion of the field from the metal and its continuous reduction, not enhancement; in front of the surface".

This remark is difficult to understand. The behaviour of both the IDP and array models is that (a) the field directly above a surface atom is higher than the "external" field somewhat above the surface, and (b) the field magnitude reduces as you move away from the atom, tending towards the external field value. This is how the field due to point charges and point dipoles behaves. I also believe that the field above the real atomic charge distribution behaves like this. The qualitative behaviour of the IDP and array models seems completely justifiable if atomic structure in the metal surface is taken into account.

The above discussion notwithstanding, it may be useful to re-emphasize that the array model is an approximation and that the basic message underlying the WPK paper — that there is a need to look again at the theoretical origin of field adsorption — is important and timely.

3. Comments on the comparison of field adsorption theory and experiment

In a fully self-consistent theory both exchange-integral induced effects and polarisation induced effects would appear, and their relative importances would be easy to determine. But at present we have two partial theories: a classical one that deals with polarisation effects; and a quantum-mechanical one that deals with exchange-integral effects, but is incapable of dealing with local polarisation effects, because the field distribution built into it has no lateral structure. Effects associated with both partial theories will be physically present in all cases, and the discussion is about relative magnitudes. It is also possible that neither partial theory alone will be able to explain the totality of experimental facts. We look at two experimental situations and compare predictive abilities.

3.1 Binding-energy values on an atomically rough surface

For the helium-on-tungsten system, for a protruding atom it is clear /7,11/ that binding energies roughly in the range 150 meV at 45 V/cm to 250 meV at 56 V/cm have been measured, and that values of this magnitude can be predicted from the Kreuzer-type theory. However, there is currently no satisfactory calculation of polarisation effects: the Tsong and Muller IDP model has known deficiencies, and the array model is not applicable.

A new, albeit crude, classical analysis of the problem (Forbes, Surface Science, to be published) leads to the following formula for the polarisation induced component, \( \Delta B \text{(conv.)} \), of the short-range field-adsorption binding energy:

\[
\Delta B \text{(conv.)} = \frac{1}{2} b^2 \left[ \frac{\Delta B}{a^2} - 1 \right] F Z
\]

\( \Delta B = \left( \Delta B^0 + \frac{2k_1b_2b_3r^2}{4\pi e_0d^2} \right) \left[ 1 - 4k_2b_2b_3/(4\pi e_0)^2d^6 \right] \)
where: $\delta_1$ is the adsorbate atom polarisability, and $\delta_2$ is the effective polarisability of a protruding substrate atom; $d$ is the separation of the atoms, and $F$ is the electric field somewhat above the surface; $\delta_1^m$ and $\delta_2^m$ are “field enhancement” factors, such that $\delta_1^mF$ is the field acting on the adatom due to the monopole component of the charge distribution, and $\delta_2^mF$ is the analogous field acting on the nearest protruding substrate atom; and $k_1$ and $k_2$ are “depolarisation factors” slightly or somewhat less than unity.

Repulsive forces are included by subtracting 50%, and dispersion forces by adding 8 meV. Taking appropriate parameter values where known, and making guesses where not, gives binding energy estimates of 75 meV at 45 V/m and 110 meV at 56 V/m. These values are somewhat on the low side, compared with experiments, but not impossibly so given the uncertainties in the estimation. The balance of argument seems to be against polarisation effects being able to explain observed binding energies by themselves, but in favour of the idea that polarisation effects may contribute significantly to observed binding energies on rough surfaces. WPK also regard this last as a possibility that needs to be investigated /2/.

In fact, the adsorption of neon in the interior of not-too-close-packed facets seems a better case for discussion. “Hopping bright spot” experiments (e.g. Ref./12/) indicate an adsorption energy of about 150 meV or more; but with array model calculations it seems virtually impossible that polarisation binding energies of this size could be predicted. Exchange-integral effects ought to be relatively more important in this case, and perhaps calculations should be carried out on large clusters having a small facet as the top surface.

3.2 The location of neon field adsorption

The “hopping bright spot” phenomenon also shows conclusively that, in the interior of a constant facet, neon is axed adsorbed. With the array model, it has been explicitly demonstrated /13/ that polarisation contributions maximise at the apex site. However, it has not yet been shown that apex adsorption is a predicted theoretical feature of exchange integral based adsorption.

In general terms we can think of the overlap of the relevant neon and metal orbitals as giving rise to a covalent donation bond, the strength of which will depend on the degree of overlap between the neon orbitals and the substrate orbitals. So, other things being equal, we might expect the bond to be stronger in the recessed site than at the apex site.

To get apex field adsorption, one or both of two things seems necessary. Either the presence of the field and potential variations above a real surface must alter the exchange-integral terms in such a fashion as to result in maximum binding energy at the apex site. Or the magnitude of the polarisation-energy terms at the apex site must be such as to overcome an opposite tendency resulting from the exchange-integral terms. The calculations necessary to resolve this issue do not yet exist, and need to be pursued.

To sum up, the idea of exchange-integral-induced effects, and their modelling by cluster calculations, seem the most significant advances in field adsorption theory for many years, and the key to a fuller understanding of the phenomenon. But it is clear that the relative importance of polarisation induced and exchange-integral induced effects have not yet been adequately established. There continues to be a need for good self-consistent calculations of field and potential variations at atomically structured surfaces. In the meantime, the question of the degree of local character in the charge distribution at a charged surface remains open, and there still seems a role for competent charged-surface models.

References