SOME MODEL CALCULATIONS FOR ADSORPTION ON TRANSITION METALS

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Perturbation theory for intermolecular forces is applied to calculate the interactions between a rare-gas atom or a hydrogen molecule and the unpaired d-electrons localized on two transition-metal atoms, the metal being nickel, palladium or platinum. The first order interaction energy is equivalent to the result of a valence-bond calculation; the second order energy consists, besides the dispersion energy, of the exchange polarization. The interaction energy, which is developed in a cluster expansion, is evaluated in the "effective electron model", using spherical Gaussian distributions for the electrons. Both the effects of physical adsorption of rare-gas atoms and dissociative chemisorption of hydrogen molecules are semi-quantitatively computed. In contrast to earlier, more approximate, calculations, it is found that the dissociative chemisorption of H₂ requires no activation energy. In this result particularly the three-body interactions play an important role.

1. Introduction

Theoretical calculations for adsorption on metal surfaces must necessarily have a rather approximate character. Experimental information about the bonding of individual atoms or molecules to the surface is only recently becoming available. Even if all data would be precisely known, the systems concerned are so complex that theoretical models must adopt some simplifying assumptions.

There is much evidence that the adsorption on transition metals is mostly localized, i.e. the adsorbate can be found in different stable positions on the surface and must surmount an energy barrier for "hopping" from one site to another. It is also very likely that the localized magnetic d-electrons in the transition metal, which are the non-bonding or "atomic" d-electrons in the valence-bond picture\(^1\,^2\)) or the anti-bonding localized d-electrons in the band model\(^3\,^4\)), play an important role in adsorption bonding. Not only is the catalytic and adsorptive activity of a transition metal correlated with the percentage of d-character in the valence-bond orbitals\(^5\,^6\)), there is also a relation with more directly measurable phenomena. The activity of alloys depends on the number of unpaired d-electrons at the surface\(^7\,^{14}\)), although Sachtler et al.\(^7\), Van der Plank\(^8\) and Cadenhead and Wagner\(^9\) have shown for Cu–Ni alloys that the explanation is not so obvious as a simple rigid-
band model would suggest. Selwood\cite{15} and Wöstien et al.\cite{16} have found that the magnetic susceptibility of “superparamagnetic” nickel crystallites is lowered by atomic hydrogen adsorption. The maximum decrease corresponds to the bonding of all unpaired d-electrons of the surface atoms with the hydrogen atoms.

The model we wish to investigate should be valid for physical adsorption, chemisorption, as well as all intermediate stages, so that we can study the adsorption of a hydrogen molecule that is first “physically” bound to a transition-metal surface, then, on coming closer to the surface, is dissociated and, finally, is adsorbed as atomic hydrogen. In many cases, for instance on nickel or platinum, this dissociative adsorption was found to require practically no activation energy.

It was found by many investigators that, particularly for chemisorption on transition metals, the local properties of the surface are more important than the collective characteristics of the metal\cite{17}. This, and the fact that too much emphasis was laid on only one aspect, limit the value of the older interpretations in terms of general geometric and electronic factors. Model calculations for adsorption on a transition metal should consider individual metal atoms, rather than use the conception of a metal as a reservoir of more or less free electrons.

2. The formalism

We shall calculate the interaction between a rare-gas atom or a hydrogen molecule and the localized unpaired d-electrons of a transition metal such as nickel, palladium or platinum. Expressions for the interaction energy that are valid for a wide range of interatomic distances, including the “physical bonding distance” as well as the smaller distances occurring in “chemical bonding”, are given by the perturbation theory described in refs. 18–23. This perturbation theory differs from the usual Rayleigh–Schrödinger perturbation theory for intermolecular forces in that it includes the effects of symmetry properties of the wave function, such as the exchange symmetry in wave functions that satisfy the Pauli principle or, in the Born–Oppenheimer approximation, the spatial symmetry of the nuclear framework.

The first order interaction energy in this perturbation series is given (in Dirac’s bracket notation) by:

\[ \varepsilon_1 = \frac{\langle \phi_0 | AV | \phi_0 \rangle}{\langle \phi_0 | A | \phi_0 \rangle}, \]

which equals the result of a valence-bond calculation. The second order energy, approximated according to Unsöld\cite{24} by semi-empirically estimating
the "average excitation energy" \( \Delta E_{av} \), reads:

\[
\varepsilon_2 = -\frac{1}{\Delta E_{av}} \left[ \frac{\langle \phi_0 | V A V | \phi_0 \rangle}{\langle \phi_0 | A | \phi_0 \rangle} - \varepsilon_1^2 \right].
\]

Besides the London–Van der Waals or dispersion energy, this second order energy contains an exchange contribution: the exchange polarization. That this exchange polarization may be important can be seen from the test calculations we have performed on \( \text{H}_2^+ \) (ref. 23).

The function \( \phi_0 \) is a product of space orbitals of the separate atoms or molecules, singly or doubly occupied. The interaction operator \( V \) consists of all electrostatic interactions between the nuclei and electrons belonging to different atoms (or molecules). The projection operator \( A \) is a special form of the antisymmetrizer. It projects antisymmetric functions that are eigenfunctions of the spin operators \( S^2 \) and \( S_z \) and possess a certain symmetry in geometric space as well. The theory of permutation groups provides us with the expressions for \( A \), which are linear combinations of permutation operators. Without explicitly deriving the space-spin functions, it yields the energy expressions corresponding to the values of the quantum numbers \( S \) and \( S_z \) as integrals over spatial coordinates only \(^{25,26}\).

Energy eigenvalues corresponding to different total spin quantum numbers \( S \) are different, even if the Hamiltonian does not contain any spin interactions. This is caused by the Pauli principle imposing different spatial distributions on functions with different \( S \) via the antisymmetry of the total wave function. Sometimes more than one space function can be found corresponding to the same \( S \). In that case, perturbation theory for degenerate states should be applied, evaluating the expressions for a matrix of projection operators \( A \) and solving a secular problem \(^{26}\).

3. Cluster expansion, effective electron approximation

The interaction energy between a number of atoms (or molecules) depends on the coordinates of all atoms. It can, however, be written in a cluster expansion as a sum of pair energies, three-body energies, etc.:

\[
E = \sum_{i<j} E_{ij} + \sum_{i<j<k} E_{ijk} + \cdots.
\]

As can be expected, and as was indeed found in some practical cases, this expansion converges, the subsequent sums in the series decreasing in magnitude. Jansen and Lombardi \(^{27,28}\) have found for rare-gas crystals, alkali halides and several other compounds that, although the pair interactions largely constitute the cohesion energy of the crystals, the three-body inter-
actions are responsible for the differences in stability between various modifications. They calculated the three-body energy relative to the pair energies in the "effective electron" model: each atom or ion having a closed-shell rare-gas configuration was represented by a single electron in a spherical Gauss function, keeping all spins parallel in order to obtain a repulsive first order energy. By semi-empirically evaluating the extension parameters of the Gauss functions, a semi-quantitative fit to the interaction energy is obtained.

In our calculations we have somewhat extended this "effective electron" approximation in order to deal with the interactions between open-shell atoms as well. Open-shell atoms are represented by a single electron in a space orbital, closed-shell atoms by a doubly occupied orbital. Different interactions occur for different spin states of the total system.

4. Models calculated

If we wish to calculate the interaction between an adsorbate, a rare-gas atom or a hydrogen molecule, and the "atomic" d-electrons of a transition metal, we should evaluate a large number of clusters. The purpose of the present investigation is to study a few of them, viz. model A for rare-gas adsorption and model B for hydrogen adsorption.

![Diagram of models A and B]

The centres a and b represent two metal atoms which are held at the nearest or next-nearest neighbour distances of the metals nickel, palladium or platinum. The centre c is a rare-gas atom in model A, c and d are two hydrogen atoms in model B. All atomic wave functions were approximated by spherical Gaussian functions of the form:

$$\varphi_s(i) = \left(\frac{\pi}{2}\right)^{\frac{3}{2}} \beta^3 \exp\left(-\frac{1}{2}\beta^2 r_i^2\right).$$

Since only interatomic integrals have to be evaluated, these single Gaussian functions can be used for semi-quantitative calculations. The extension parameters $\beta$ of the rare-gas and hydrogen atoms were chosen such that the atomic dipole polarizabilities (which are proportional to $\langle \sum_i r_i^2 \rangle$) and, therewith, the second order dispersion energy, are calculated correctly. According to Jansen, the $\beta$-values for rare-gas atoms were somewhat modified in the
calculation of the first order energy (as indicated in the figure captions). For representing the localized metallic d-electrons the choice of spherical Gaussians seems somewhat curious. However, if all d-orbitals were exactly degenerate, the effective electron would indeed have a spherically symmetric distribution. Diffraction experiments with polarized neutrons on nickel\(^{30,31}\) have shown that the splitting between the d-bands of different symmetry is of the same magnitude as the thermal energy at room temperature (0.6 kcal/mole). Although this splitting might be larger at the surface, we have assumed that it is still small compared with the adsorption energy so that, in the first instance, we may represent the unpaired metallic d-electrons effectively by spherical functions\(^*\). Measurements of the form factor of the magnetic d-electrons in nickel\(^{34}\) demonstrate that Gaussian functions are quite correct. The extension parameters \(\beta\) of the metallic electron functions were found by equating the overlap between two metal atoms at nearest or next-nearest neighbour distance to the values that were calculated with the radial parts of atomic self-consistent field functions\(^{35-37}\)).

The “average excitation energy” in the Unsöld second order energy, which increases with decreasing interatomic distance\(^{18,23,38}\), was written as:

\[
\Delta E_{av} = \Delta E_{av} (1 + c\Delta^2)
\]

with, in model A:

\[
\Delta E_{av} = \text{first + second ionization energy of the rare-gas atom + twice the ionization energy of a d-electron in a metal atom,}
\]

\[
\Delta^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2,
\]

and in model B:

\[
\Delta E_{av} = \text{twice the ionization energy of a hydrogen atom + twice the ionization energy of a d-electron in a metal atom,}
\]

\[
\Delta^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{ad}^2 + \Delta_{bc}^2 + \Delta_{bd}^2 + \Delta_{cd}^2.
\]

A comparison of the interaction energy between two hydrogen atoms or two rare-gas atoms with the known results shows that the best value of the numerical constant is approximately equal to 4. It was verified that the particular approximation which we used for \(\Delta E_{av}\) does not significantly influence the results of these calculations. The numerical values of the parameter

\* We have also carried out pilot calculations with d\(_{\perp}\) orbitals. However, as the results were more complex and, consequently, more difficult to interpret, a specific choice of d-orbitals for these first calculations did not seem justified. If, in more elaborate calculations, one would like to account for the differences in symmetry occurring on different surfaces\(^{32}\), one could, for instance, use linear combinations of spherical orbitals, possibly with displaced centres, in the manner of Preuss\(^{33}\). This would reduce the mathematical problems to those that have already been solved in these calculations.
$\beta$ and the atomic ionization energies are listed in table 1 (1 atomic unit of distance = Bohr radius $a_0 = 0.53$ Å; 1 atomic unit of energy = 27.2 eV = 626 kcal/mole).

<table>
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<tr>
<th></th>
<th>H</th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Ni (3d)</th>
<th>Pd (4d)</th>
<th>Pt (5d)</th>
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<tr>
<td>$\beta (a_0^{-1})$</td>
<td>0.71</td>
<td>1.17</td>
<td>0.80</td>
<td>0.46</td>
<td>0.39</td>
<td>0.33</td>
<td>0.88</td>
<td>0.75</td>
<td>0.70</td>
</tr>
<tr>
<td>Ionization energy (a.u.)</td>
<td>0.5</td>
<td>I: 0.9</td>
<td>I: 0.8</td>
<td>I: 0.6</td>
<td>I: 0.5</td>
<td>I: 0.4</td>
<td>II: 2.0</td>
<td>II: 1.5</td>
<td>II: 1.0</td>
</tr>
</tbody>
</table>

Within the framework of the model described above the first and second order interaction energies were calculated exactly. All multicentre integrals with Gaussian functions were computed. Especially for the integrals occurring in the second order energy, which are more complicated than those which one usually encounters in variational calculations, the methods of Zimering$^{39}$ and Roberts$^{40}$ were invoked. Also the writing out and the sorting of the numerous integrals were performed directly by a computer in the way described in ref. 26.

5. Results

5.1. RARE-GAS ADSORPTION

The results of the calculations on model A are given in figs. 1–5. The interaction energy is plotted as a function of the height of the rare-gas atom above the metal atoms. Only isosceles triangles were considered. The middle curves

Fig. 1. First and second order interaction energy of the system $\beta$ (first order) 30% larger than $\beta$ (second order).
represent the sum of the pair energies. The pair energy of the two metal atoms depends on their spins being anti-parallel or parallel, corresponding to spin 0 or 1 of the total system. However, this pair energy is small compared with the pair interactions between each of the metal atoms and the rare-gas atom, which are independent of the total spin. Consequently, the total pair energy is practically spin-independent. As expected, the first order pair energy is repulsive, the second order attractive, their sum yielding a typical curve for physical adsorption. The calculated "heats of adsorption" of different

Fig. 2. First and second order interaction energy of the system

\( \beta \) (first order) 20\% larger than \( \beta \) (second order).

Fig. 3. First and second order interaction energy of the system

\( \beta \) (first order) 10\% larger than \( \beta \) (second order).
Fig. 4. First and second order interaction energy of the system $\beta$ (first order) equal to $\beta$ (second order).

Fig. 5. First and second order interaction energy of the system $\beta$ (first order) 10\% smaller than $\beta$ (second order).

Rare gases are listed in Table 2. (The experimental values reported in the literature\textsuperscript{41} are $\sim 5$ kcal/mole for krypton and xenon on nickel.) The second order exchange force, the exchange polarization, is repulsive, thus lowering the binding energy by approximately 20\%. The equilibrium distance increases in the order:

$$\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe},$$
as does the binding energy. (The increase of the binding energy is practically not obtained if, less accurately, one used a single parameter $\beta$ for the rare-gas atoms in first and second order.)

The three-body interactions are important, especially in first order. They add an attractive effect when the spins of the metal electrons are anti-parallel, and a (smaller) repulsion when the spins are parallel. This indirect, mainly exchange, interaction between the metal spins via the rare-gas atom, which is not very important at the physical bonding minimum, can become much larger than the direct exchange interaction between the metal atoms for smaller distances. For neon the effects are smaller than for argon, krypton and xenon; for helium they almost vanish.

5.2. HYDROGEN ADSORPTION

For model B the interaction energy is calculated for the ground state ($S = 0$) as a function of both the height of the hydrogen atoms above the metal atoms and the distance between the hydrogen atoms. Figs. 6–8 show the various contributions to the interaction energy as a function of the distance between the hydrogen atoms for different heights. Figs. 9 and 10 contain the same results as figs. 6 and 8. They are now represented in a contour map as curves of equal energy which are functions of variations in both distances. The dashed line corresponds to the line of minimum energy which is followed by a hydrogen molecule approaching the two metal atoms.

These results show that for the metal atoms at nearest-neighbour distance the pair interactions alone would cause a strong attraction of the hydrogen atoms, which are drawn into the surface, but do not change their equilibrium distance compared with the isolated molecule. The second order “physical”

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**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>Xe</th>
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<th>Ar</th>
<th>Ne</th>
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<td>4</td>
<td>3</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>Pd</td>
<td>4.7</td>
<td>4.5</td>
<td>4.3</td>
<td>3.7</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>4.2</td>
<td>4.1</td>
<td>4.0</td>
<td>3.4</td>
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</tr>
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<td>6</td>
<td>5.5</td>
<td>4.5</td>
<td>2.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Fig. 6. First and second order pair interaction energy of the system

Fig. 7. First and second order pair + three-body energy of the system
attraction passes continuously to a strong first order "chemical" attraction which, for the distances of interest, dominates over the second order effects. (Note that the energy-scale values in these figures are much larger than in figs. 1–5.) When the cluster becomes more compact, the three- and four-body interactions become important. The three-body energy is repulsive and increases with decreasing distance between the hydrogen atoms. Therefore, when the height of the hydrogen atoms above the metal atoms is smaller than $2a_0$, the pair attraction between the hydrogen atoms is compensated by the three-body repulsion with the metal atoms; the hydrogen molecule can dissociate without an activation energy, the atoms moving apart to be separately bound to the metal atoms. The four-body interactions generally counteract the three-body effects, but they are smaller so that the results described are maintained if also the four-body energy is added.

Figs. 11 and 12 demonstrate that the effects of the three- and four-body interactions are much less marked if the metal atoms are at next-nearest neighbour distance.

The results of these calculations can be compared directly with those of Sherman et al.\textsuperscript{42,43} and of Okamoto et al.\textsuperscript{44} (see also ref. 45). These authors have also computed the interaction energy between a hydrogen molecule and two nickel atoms in the same model as ours. Their expression for the
Fig. 9. Contour map of the pair interaction energy of the system

Fig. 10. Contour map of the total interaction energy of the system
Fig. 11. Contour map of the pair interaction energy of the system

Fig. 12. Contour map of the total interaction energy of the system
interaction energy, which was obtained by the valence-bond method, differs from our first order energy in the following points:
- the overlap and the multiple-exchange integrals between different atoms were neglected;
- the Coulomb integrals and the single-exchange integrals which remain, were estimated from empirical Morse curves for the pair bonds between the atoms. This estimation was based on the assumption of a fixed percentage of Coulomb energy, independent of the interatomic distance.

![Figure 13. Total first and second order interaction energy of the system Pt-H along the "reaction coordinate". (----) effect of localized unpaired d-electrons; (.....) repulsive effect of bonding and conduction electrons added.]

Without the aid of an electronic computer, however – the calculations were made in 1932 – these approximations were practically inevitable.

The results are rather different from ours: Sherman et al. and Okamoto et al. find that the hydrogen atoms, on approaching the metal atoms, stay practically at the equilibrium distance of the isolated molecule and would require a large activation energy to dissociate – a result which resembles ours if we consider pair interactions only. Further, the adsorption energy they calculated is much lower than ours.

The results of our calculations can also be related to the hypothetical curve for non-activated dissociative adsorption of H₂ as given, for example, by De Boer⁴⁶. His figure should be compared with our fig. 13. The full line
in fig. 13 was obtained by plotting the total interaction energy (from figs. 8 and 10) of a hydrogen molecule approaching two metal atoms at nearest neighbour distance along the line of minimum energy. The physical bonding, which is very weak and passes continuously to the strong chemical bond, cannot be observed explicitly in this curve. The adsorption energy for dissociative hydrogen adsorption, which is also listed in table 3, is too high (the experimental values for the initial heats of adsorption on Ni, Pd and Pt being 29–32, 27 and 28 kcal/mole$^{47}$). This result is to be expected since only the effect of unpaired metal d-electrons was taken into account. The repulsive effect of the bonding d-electrons and conduction electrons can be computed approximately, within a four-center model, by replacing the single electron on each metal atom by a doubly occupied, more delocalized orbital. If the three- and four-body effects are small in this case, roughly the same effect is obtained on using model B, holding the spins on the metal atoms parallel to those on the hydrogen atoms, for instance, by calculating the state with $S = 2$. The calculation of the repulsive interaction between the hydrogen atoms and the “closed-shell” metal atoms in the latter model (with extension parameters $\beta$ for the metal orbitals that are three times smaller than the values of table 1) showed that indeed the three- and four-body interactions are small. If this repulsion is added to the interaction energy calculated before, the adsorption energies are lowered as shown in table 3, and the dashed line in fig. 13 is obtained. The small activation barrier for adsorption that can be observed from this line is due to the fact that the very approximate computation of the repulsive interaction probably overestimates the extension of the metallic bonding and conduction electrons, particularly in the direction of the “surface”.

6. Conclusions

Despite the simplifications introduced into these models, some interesting results were obtained. Both the physical adsorption of rare gases and the dissociative chemisorption of $\text{H}_2$ can be explained semi-quantitatively. In contrast to earlier calculations it was found that the dissociative chemisorp-
tion of hydrogen molecules on Ni, Pd or Pt requires practically no activation energy. Especially the three-body interactions play an important role in this result.

The present model calls for several refinements. Instead of just considering two metal atoms at nearest or next-nearest neighbour distance, the interactions with all surface atoms within a certain domain or even with a few outer layers should be calculated. In this way the characteristics of adsorption on different surfaces can be obtained. Possibly it is necessary to allow for the different crystallographic environment in various surfaces by using d-orbitals of different symmetry for the metal atoms. Also the effects of increasing surface coverage, in which probably the many-body interactions between the adsorbate atoms (or molecules) and the metal atoms are important, may be considered. For adsorption of $\text{H}_2$, for example, the results of several possible manners of impact on the surface can be studied. The influence of the conduction electrons or surface potentials, also in the presence of strong electric fields (as occurring in Field Ion Microscopy), may be investigated. All these calculations, however, which seem within the limit of the present practical possibilities, and some of which have already been performed by different authors (see the survey in ref. 26), are necessarily approximate in some way or other, for which reason they require a thorough experimental verification.

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Discussion

J. A. A. Ketelaar (University, Amsterdam)

One would deduce from the fact that the H–H distance at the energy minimum of about 9 \( a_0 \) is much larger than the Pt–Pt distance of 5 \( a_0 \), that a still lower energy would be found for isolated H atoms on a Pt atom. Could you take from your calculations just intermediate
results to calculate this energy as $1 \times (\text{Pt-H}) + 6 \times (\text{Pt-Pt-H}) + 6 \times (\text{Pt-Pt})$ interaction energies for a H atom on a Pt atom in a (111) surface.

A. VAN DER AVOIRD

For the calculated configurations the total pair interaction between Pt and H atoms is attractive, whereas the sum of three- and four-body interactions is repulsive. This would mean indeed, as far as this model can predict, that an isolated H atom on a Pt surface is most stable, and therefore that the adsorption energy would decrease with increasing surface coverage. However, as you observe, this should be tested on a model with more Pt atoms. In such extended models, in which I intend to investigate the effect of various crystallographic surfaces, the total interaction energy should again be developed in a cluster expansion. It might appear that, besides the pair and three-body interactions, also higher-order contributions are important.

H. G. E. Schütz (Technical University, Munich)

In so far as I understood your model, an activation barrier did not appear in your calculation, but may be found in principle, e.g., for a greater distance between the Pt atoms. In the case of a pure germanium surface, it is known that no chemisorption of molecular $\text{H}_2$ occurs, though atomic hydrogen is chemisorbed immediately. It should be very interesting, therefore, to apply your theoretical approach to a germanium surface with dangling bonds.

A. VAN DER AVOIRD

One can substitute the parameters of a germanium surface into this model. However, if the correct results would not be obtained I would not be too disappointed. Whether an activation barrier occurs or not depends on the balancing of several effects. If one just calculates these effects in a very approximate way, as I did, and moreover considers them as additive, it might be that the result is not correct in all cases. Therefore this model should be refined.

G. C. A. Schuit (Technical University, Eindhoven)

If one changes the “effective electron” number per transition metal atom, e.g., from 0 to 1 (as you did) to 2, could one “see” in a simple way what would happen? For instance, no adsorption energy – strong adsorption energy – no adsorption energy.

A. VAN DER AVOIRD

If one takes 0 electrons on the metal atoms in this model, no interaction with hydrogen would occur; in the case of 2 electrons a repulsion arises. Bonding can only be calculated if one takes electron transfer into account. This effect, which in our model with 1 electron per metal atom would imply ionic terms, was not included in the calculations, as it appears from earlier studies that the ionicity of the metal-hydrogen bond is probably quite low.

The result that in this model maximum bonding occurs with one electron per metal atom would lead to the conclusion that the chemisorption bond is correlated with the number of unpaired d-electrons at the surface atoms. A more detailed evaluation of the
effect of the filling of the d-band requires the extension of the model calculations to d-type orbitals on the metal atoms.

A. S. PORTER (Albright and Wilson, Warley)
Are you able to make any prediction from your model about the effect of adsorption on the surface conductance?

A. VAN DER AVOIRD
I am not, from this model. I consider the conduction electrons as more or less delocalized, but I have no criterion for the conductivity.