Calculation of Interactions Between Adsorbates on Transition Metal Surfaces

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We present an electronic calculation of two- and three-body interactions in chemisorbed layers. The interaction energies are obtained in a self-consistent way within the tight-binding formalism which includes electron correlations and interatomic pairwise repulsion terms. Numerical results for Re$_2$ and Re$_3$ on W(110) are compared with recent experimental data.

1. Introduction

The nature of interactions between adsorbates has attracted much attention over the past few years due to its importance for the structure of adsorbed layers and chemical reactions between adsorbed species. While low energy electron diffraction (LEED) studies [1] together with Monte-Carlo calculations [2] of adsorbate phase diagrams provide a reasonable estimate of their magnitude, only recently these interactions could be determined more directly by using the field ion microscopy (FIM) [3]. These recent experiments reported a repulsive two-body and an attractive three-body interaction between Re atoms adsorbed on W(110). This behavior has not yet been understood.

Since the pioneering work of Grimley, who investigated the asymptotic behaviour of indirect interactions between two adsorbates [4], various calculations of such interactions have been performed and reviewed in an instructive article by Einstein [5]. In contrast to these calculations, which are mainly interested in the general behaviour of indirect interactions in model systems, we present a self-consistent calculation for the interaction within adsorbed dimers and trimers, take care of correlation energies and consider adsorbate relaxations. While this work was in progress, we got

aware of a recent theoretical study of similar systems, which, by using some model assumptions, comes to similar conclusions [6].

2. Theory

We define the interaction w_n(i) between n adsorbed atoms of type A in a geometrical arrangement i (given by their positions) on a metallic substrate M by

$$w_n(\mathrm{i}) = E_{\mathrm{tot}}(\mathrm{A}_n(\mathrm{i})/\mathrm{M}) - E_{\mathrm{tot}}(\mathrm{A}_n(\infty)/\mathrm{M}) \,. \tag{1}$$

E_{tot} is the total energy of the adsorption system (with respect to isolated atoms) and can be decomposed into band structure correlation and repulsive parts as

$$E_{\mathrm{tot}} = E_{\mathrm{bs}} + E_{\mathrm{corr}} + E_{\mathrm{rep}} \,. \tag{2}$$

In the following these terms are briefly discussed; the details will be published elsewhere [7]. E_{bs} is a one-electron energy based on an Anderson-type Hamiltonian and given by

$$E_{\mathrm{bs}} = \sum_{i,\alpha,\sigma} \int_{-\infty}^{E_F} (E - \varepsilon_{i\sigma}^{\alpha 0}) N_{i\sigma}^{\alpha 0}(E)\,\mathrm{d}E \,. \tag{3}$$

Here, i denotes the site, α the orbital and σ the spin. The single-site energies $\varepsilon^{\alpha 0}$ are determined in such a way that the

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global charge neutrality is guaranteed. We use distance de-
pendent Slater-Koster parameterized hoping integrals. Lo-
cal densities of states $N_{i\sigma}^{z0}(E)$ are calculated by using the
recursion technique [8].

The correlation effects are treated within the Hubbard
model by perturbation theory up to second order in U/W,
where U is the Coulomb integral and W is the bandwidth
[9]. In the term E_{corr}, we include the Hartree-Fock electron-
electron contribution, which is of first order in U, as well
the second order term in U^2, which is the first proper con-
tribution to the correlation energy, this latter one is related
to the "virtual" excitations of electrons.

The repulsive term E_{rep} accounts mainly for the inter-
nuclear and close-shell repulsion and corrects double-count-
ing terms. It is modeled by pairwise Born-Mayer interac-
tions [7] whose distance-dependence can be obtained from
bulk elastic constants. Including these repulsive terms allows
also to consider adsorbate relaxations by minimizing the
total energy.

Applying our formalism to Re_2 and Re_3 on $W(100)$, we
use electronic parameters given elsewhere [10]. The $W(110)$
substrate is assumed to be unrelaxed and unreconstructed
[10]. Direct interactions between Re adatoms are considered
in nearest and second nearest sites. Local densities of states,
which are correct up to the 8th moment, are evaluated at
the adsorbate and all neighbouring substrates sites. These
sites are also considered in a charge self-consistency pro-
cedure to maintain the global charge neutrality. For a given
adsorption geometry, adsorbate relaxations and the corre-
sponding energies have been determined by minimizing the
total energy of the system.

The assumption of a vanishing correlation term E_{corr} in
Eq. (3), obtained by setting the intraatomic Coulomb inte-
gral $U = 0$, results in strongly attractive Re_2 interactions on
$W(110)$ in contrast to the experiment [3]. For a vanishing
Coulomb integral U, nearest neighbours Re_2 dimer would
be stable, with an energy -1.13 eV. For increasing U, this
binding diminishes, uniformly, and the interaction becomes
repulsive for $U \geqslant 1.6$ eV. This value has been kept through-
out the calculation. This procure is similar to that adopted
by Bourdin et al. [6].

3. Results

The results of our calculation, the Re_2 interactions on $W(110)$ as
a function of the adsorbate separation, are given in Fig. 1b. The
corresponding adsorption sites are shown schematically in Fig. 1a.
For all configurations we studied, each Re atom has two W atoms
as nearest-neighbours and two W atoms as next-nearest-neigh-
bours. Unfortunately we were not able to study systematically the
multi-dimensional interaction energies, due to the prohibitive com-
puter time necessary for it. We observe an oscillatory behaviour of
the distance-dependence pair interactions as suggested already by
Grimley [4]. The dashed area in Fig. 1 corresponds to sites outside
the exclusion zone observed in the experiment of Fink and Ehrlich
[3]. We found a dimer repulsion up to the 3th nearest neighbour
site and a weak dimer attraction at longer distances. Hence the
calculated exclusion zone is smaller than the observed one. This
discrepancy could be a consequence of a slightly exaggerated charge
transfer which strongly influences the correlation energies. The val-
ues of the first and second nearest neighbour interactions can be
understood within a simple electronic model based on the second
moment approximation [6, 7]. This model, of course, cannot de-
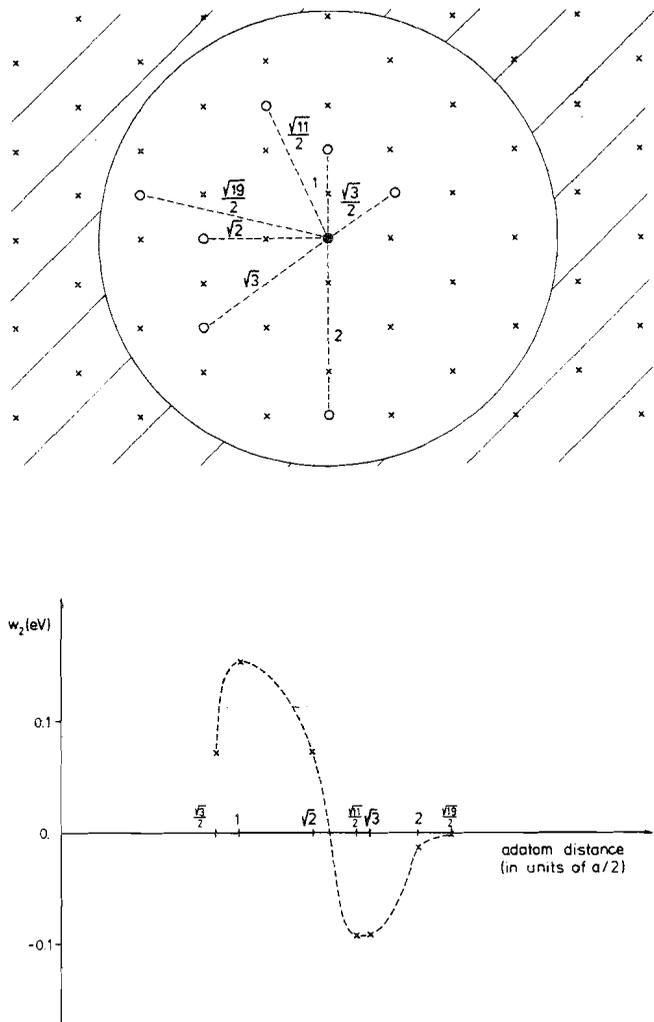scribe the long-range behaviour of the interaction.

Fig. 1
Dimer interaction w_2 in $Re_2/W(110)$. a) Schematic drawing of the
surface geometry. Surface layer W atoms are marked by ($\times$), Re
adsorbates by ($\bigcirc$). b) Interaction energies as a function of adatom
distance (in units of the substrate lattice constant $a/2$). The hatched
area marks the excluded region around a Re atom observed in
Ref. [3]

In Fig. 2 we present the interactions in Re_3 on $W(110)$. We con-
sider a "pointed" (P) arrangement with three direct bonds, an
"open" (O) and a "linear" (L) arrangement with two direct bonds
and show the corresponding geometry in Fig. 2a. As can be inferred
from Fig. 2b, where we show the corresponding interaction energies,
the L trimer is most stable, followed by the O trimer, and the P
trimer is unstable.

The value of the calculated interaction energy -0.18 eV of
L-Re_3 agrees with the observed value [3] -0.25 ± 0.1 eV. The
unstable P-Re_3 has not been observed. It is interesting to note that
neither a simple electronic model based on the second moment
approximation with local charge neutrality and correlation energies
[6] nor a thermodynamic consideration [3] can explain the relative
stabilities of the considered trimers. They predict the most compact
P-Re_3 to be most stable, in contrast to our results and to experi-
mental evidence.

With the electronic parameters used, we also studied the impor-
tance of adsorbate relaxations on the interaction energies. In gen-
eral, we found that the inclusion of correlation energies suppresses
adsorption bond contractions from -9% to $-1\% \ldots -4\%$. The
corresponding relaxation energies are small and nearly cancel in
the difference in Eq. (1).

The correlation effects are expected to be the most important for
a "half-occupied" band, a case which corresponds to those transi-
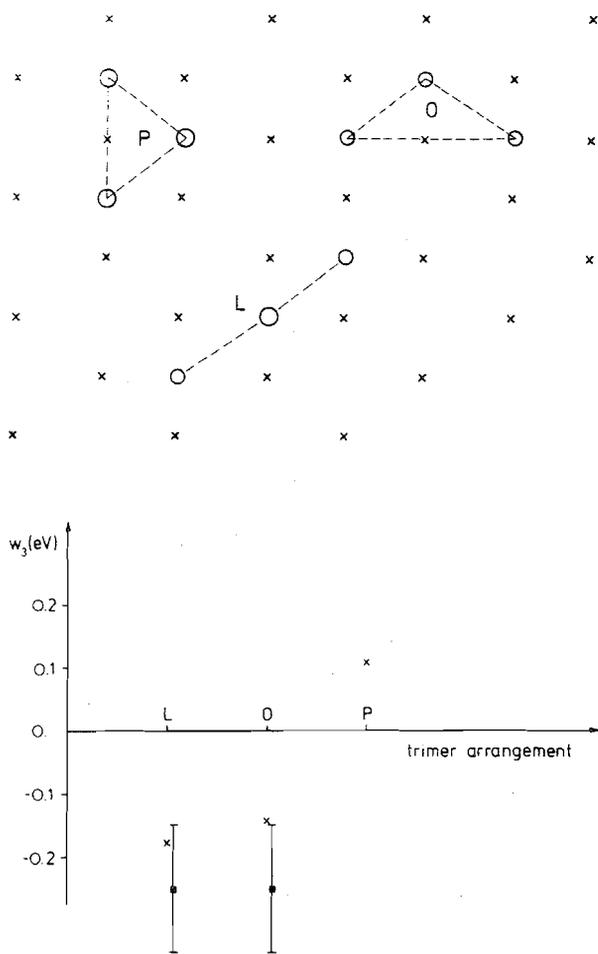
Fig. 2
Trimer interactions w_3 in $Re_3/W(110)$. a) Schematic drawing of the atomic arrangement. b) Interaction energies for different arrangements. The experimental data (■) are taken from Ref. (3)

mention that the small value of the ratio of the Coulomb integral U to the bulk bandwidth W ($U/W < 15\%$) justifies a perturbation theory treatment of correlation energies. We conclude that Re interactions observed on W(110) can only be explained by a model which considers correlation effects.

We would like to point out that neglecting direct interactions between neighbouring adatoms, as done in early calculations quoted in Ref. [5], automatically leads to repulsive Re_2 interactions, even in absence of correlation terms. From a detailed investigation we concluded that (when neglecting correlation energies) in order that the dimer interaction is repulsive, the hopping integrals between the adatoms should be reduced by nearly 1/2 with respect to their bulk value to a value appropriate for the free molecule.

We also found that a proper determination of the charge distribution in the system (by applying the global charge neutrality condition) is especially important in cases such as Re_3, where charge transfers mainly between adatoms can affect the relative stability of different geometries.

With the exception of Re, other 5d adsorbates show attractive dimer interactions on W of a magnitude which is generally comparable with Re trimers [12]. As pointed out previously [5], trimer interactions cannot be neglected in the interpretation of phase diagrams observed for these systems.

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tion metals located in the middle of the periodic table, such as W and Re. In a simple model [6,9], the correlation term is found roughly inversely proportional to the square root of the number of neighbouring atoms; so it is most important for monomers and least important for compact adatom arrangements. In the case of a Re monomer, $U = 0$ eV gives a calculated adsorption energy of 5.94 eV; using $U = 1.6$ eV, increases the adsorption energy to 7.8 eV. This increase in the heat of adsorption improves the agreement with the experimental results [11]. For a Re_2 dimer where the two Re atoms are nearest-neighbours, the inclusion of the correlation terms counterbalances the band energy gain to the additional bond between the two Re atoms. Let us remark that the interaction energy $w_2 (\sqrt{3}/2)$ found in absence of correlation terms (-1.13 eV), in disagreement with the experimental data, is unphysically large; a similar result is found in the case of R_3 trimers on W(110). Let us