MULTI-ADATOM INTERACTIONS ON METAL SURFACES

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We present an electronic calculation of interactions between impurities adsorbed on transition metal surfaces. The interaction energies are determined in a self-consistent way within the tight-binding formalism which includes correlation and interatomic repulsion terms. We apply our formalism to Re_2 and Re_3 on W(110) and compare the numerical results with recent experiments.

1. Introduction

The determination of interactions in adsorbed layers has attracted much attention in recent years due to their importance for the crystal growth, interface formation and heterogeneous catalysis. Experimental information about two-, three- and many body interactions can be extracted, at least in a qualitative way, from adsorbate superstructures on single crystals observed by low energy electron diffraction (LEED) [1], the coverage dependence of the heat of adsorption in thermal desorption spectroscopy (TDS) [2], and most directly from (pair-, trio-) distribution functions and lifetimes for dissociation observed directly in field ion microscopy (FIM) [3]. So far, however, only few quantitative data have been reported [3,4]. The magnitude of adsorbate interactions can also be estimated from the comparison of order–disorder phase diagrams calculated in lattice gas models [5] and observed by LEED. Since the choice of interaction energies which explain a phase diagram need not be unique, the only reliable way to determine and understand such interactions is from total energy calculations.

Theoretical calculations of adsorption systems have achieved a high level of sophistication in the treatment of single impurities [6] or completely ordered overlayers [7]. Due to the low symmetry of the problem, mainly model calculations have been performed to determine the interaction between few

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(two-, three, ...) adsorbed impurities. Theoretical approaches used until 1978 have been compiled in a review article by Einstein [8]. In his pioneering work, Grimley showed that the indirect interactions between two adsorbates through a metal substrate show a damped oscillatory behaviour in the asymptotic limit [9]. Einstein and Schrieffer gave first realistic results for dimers on a single-band simple cubic lattice [10]. Burke showed in his calculation for impurities on a multiband bcc substrate (of the same type as the adsorbate) the dependence of the interactions on the Fermi energy [11]. From their calculations of hydrogen on nickel, Schönhammer et al. concluded that correlation terms contribute only negligible amounts to indirect interactions [12]. Among the more recent calculations Muscat treated H interactions on Fe in the embedding technique [13] and Nordlander and Holmström by an effective medium theory [14]. These schemes can be extended to treat three- and many-body interactions.

In the next section we expose the model used here. Within a tight binding formalism, repulsive energies and electron correlations are taken into account. We consider direct and indirect interactions between adsorbates and we determine, for a given adsorption geometry, the equilibrium positions and the corresponding energies in a self-consistent way (the global charge neutrality is guaranteed). We make quantitative predictions for Re_2 and Re_3 on $W(110)$ and draw conclusions for other systems.

2. Theory

The interaction $w_n(i)$ between n adsorbed atoms of type A in a geometrical arrangement i (defining their mutual positions) on a metal substrate M is defined by

$$w_n(i) = E_{tot}(A_n(i)/M) - E_{tot}(A_n(\infty)/M). \tag{2.1}$$

E_{tot} is the total energy of the adsorbate–substrate system (with respect to isolated atoms) and $A_n(\infty)$ denotes adatoms separated by an infinite distance. The total energy can be decomposed into a band structure, a correlation and a repulsive part, as

$$E_{tot} = E_{bs} + E_{corr} + E_{rep}. \tag{2.2}$$

The band structure energy can be obtained by using an Anderson-type tight-binding Hamiltonian

$$H = \sum_{i,\alpha,\sigma} \left(\epsilon_{i\sigma}^{\alpha} n_{i\sigma}^{\alpha} - \epsilon_{i\sigma}^{\alpha 0} n_{i\sigma}^{\alpha 0} \right) + \frac{1}{2} \sum_{i,j,\alpha,\beta,\sigma} t_{ij}^{\alpha\beta} c_{i\sigma}^{\alpha+} c_{j\sigma}^{\beta}, \tag{2.3}$$

where i and j can denote both the adsorbate or metal substrate sites, α and β the corresponding orbitals and σ the spin. c^+ (c) are the creation (annihila-

tion) operators of electrons in the corresponding states, ϵ_i (ϵ_i^0) are the single-site energies in the adsorption system (of the isolated atoms) and t_{ij} are the hopping integrals between neighboring sites i and j.

The band structure energy is given by

$$E_{bs} = \sum_{i,\alpha,\sigma} \int_{-\infty}^{E_F} (E - \epsilon_{i\sigma}^{\alpha 0}) N_{i\sigma}^{\alpha}(E) \, dE, \tag{2.4}$$

where the local density of states $N_{i\sigma}^{\alpha}(E)$ of the orbital α and spin σ at the site i is given by

$$N_{i\sigma}^{\alpha}(E) = -\frac{1}{\pi} \, \text{Im} \, G_{ii,\sigma}^{\alpha\alpha}(E), \tag{2.5}$$

and the site occupancy is

$$\langle n_{i\sigma}^{\alpha} \rangle = \int_{-\infty}^{E_F} N_{i\sigma}^{\alpha}(E) \, dE. \tag{2.6}$$

The conservation of electrons is taken care of by the global charge neutrality condition

$$\sum_{i,\alpha,\sigma} \langle n_{i\sigma}^{\alpha} \rangle = \sum_{i,\alpha,\sigma} n_{i\sigma}^{\alpha 0} = \text{const.} \tag{2.7}$$

The correlation energy has been given up to the second order perturbation theory by [15]

$$E_{corr} = \sum_i \left\{ \frac{U_i}{2} \left[\left(\sum_{\alpha,\sigma} \langle n_{i\sigma}^{\alpha} \rangle \right)^2 - \sum_{\alpha,\sigma} \langle n_{i\sigma}^{\alpha} \rangle^2 \right] - \frac{U_i^2}{2} \sum_\sigma \left[2(2l+1)^2 - (2l+1) \right] \right.$$
$$\times \int_{E_F}^{\infty} dE_1 \int_{E_F}^{\infty} dE_2 \int_{-\infty}^{E_F} dE_3 \int_{-\infty}^{E_F} dE_4$$
$$\left. \times \frac{\langle N_i(E_1) \rangle \langle N_i(E_2) \rangle \langle N_i(E_3) \rangle \langle N_i(E_4) \rangle}{E_1 + E_2 - E_3 - E_4} \right\}. \tag{2.8}$$

Here, U_i is the intra-atomic Coulomb integral and $\langle N_i(E) \rangle$ is the renormalized local density of states (averaged over the $(2l+1)$ orbitals α, $l = 2$ for d-electrons) given by

$$\langle N_i(E) \rangle = \frac{1}{2(2l+1)} \sum_{\alpha,\sigma} N_{i\sigma}^{\alpha}(E). \tag{2.9}$$

The term E_{rep} in eq. (2.2) is supposed to consist of pairwise repulsive energies between atoms,

$$E_{rep} = \sum_{i<j} E_R(r_{ij}), \tag{2.10}$$

which account mainly for the internuclear and closed-shell repulsion and are modeled by Born–Mayer interactions as

$$E_R(r) = E_R(r_0) \exp\left[-p(r/r_0 - 1) \right]. \tag{2.11}$$

Here, r_0 is the equilibrium nearest neighbour distance in the bulk. The equilibrium geometry is obtained by minimizing the total energy with respect to atomic positions,

$$E_{tot}\{x_i, y_i, z_i\} = \min. \tag{2.12}$$

Applying this formalism to the interesting case of transition metal impurities on a transition metal substrate, we consider five degenerate d-orbitals at each site and assume an exponential distance-dependence of the Slater–Koster parameterized hopping integrals, as [16]

$$t(r) = t(r_0) \exp\left[-q(r/r_0 - 1)\right]. \tag{2.13}$$

Usually, the self-consistency is taken care of by shifting the diagonal terms of the Hamiltonian given in eq. (2.3) as

$$\epsilon_{i\sigma}^\alpha = \epsilon_{i\sigma}^{\alpha 0} + \Delta\phi_i^\alpha + \sum_{\beta,\sigma} U_{ii}^{\alpha\beta} \Delta\langle n_{i\sigma}^\beta \rangle + \sum_{j \neq i, \beta, \sigma} V_{ij}^{\alpha\beta} \Delta\langle n_{j\sigma}^\beta \rangle, \tag{2.14}$$

where $\Delta\phi_i$ is the change in crystal field, $U_{ii}(V_{ii})$ are the intra- (inter-) atomic Coulomb integrals and $\Delta\langle N_i \rangle$ are the charge transfers at the corresponding sites. The determination of the values of U and V for a given system is delicate. Since $V \approx \frac{1}{8} U$ [17] and since charge transfers on the neighbouring sites of a given atom compensate to a large extent, the contribution of the last term in eq. (2.14) has been found negligibly small when compared with other terms. Due to uncertainties in the determination of U and $\Delta\phi_i^\alpha$, we determine the diagonal elements of the Hamilton operator directly from a global charge neutrality condition.

The self-consistency procedure, which implicitly accounts both for changes in the crystal field and the Coulomb interactions, consists of two stages. First, for a clean surface, the d-level ϵ_S of the topmost layer atoms is adjusted to obtain global charge neutrality, eq. (2.7). Next, considering a single adsorbed impurity, its d-level $\epsilon_A = \epsilon_1$ is shifted in the same way, while ϵ_S is kept fixed. A similar procedure is applied in the case of a dimer, there the adsorbate level $\epsilon_A = \epsilon_2$ depends on the adatom distance. Hence, the determination of ϵ_S, ϵ_1 and ϵ_2 is parameter-free. In the trimer and more complicated adsorbate structures, shifts of two and more levels have to be considered. In contrast to requiring local charge neutrality, this procedure yields reasonable charge transfers and Friedel charge oscillations in subsequent substrate layers.

In the following section we apply our formalism to interactions between Re atoms adsorbed in W(110).

3. Calculation of interactions in Re$_2$ and Re$_3$ on W(110)

In order to investigate the reliability of our formalism, we calculate interactions between two and three adsorbed Re atoms on W(110) and compare the

results with recent experimental data [3]. In this system it seems especially interesting to find microscopic understanding of the observed repulsive "duo" and attractive "trio" interactions between two and three adsorbed Re atoms, respectively.

While our investigation was in progress, we became aware of a recent theoretical study of the same systems [18]. We find it noteworthy that these authors, using a simplified electronic model, find essentially the same reason for the behaviour of $Re_n/W(110)$ as our more sophisticated calculation.

In our calculation, only the d-electrons are taken into account [19] and we used the Slater–Koster parameterized hopping integrals which have been adjusted to the bulk band structure [20]. For the nearest (second nearest) neighbours in W we used $dd\sigma = -1.4456$ eV (-0.8757 eV), $dd\pi = 0.7984$ eV (0.4834 eV) and $dd\delta = 0$ eV (0 eV). We assumed $q = 3$ in eq. (2.13) for the distance dependence of the hopping integrals and a band filling of 4.6 electrons [16] for W. We used $U = 1.6$ eV for the intra-atomic Coulomb integral and for the repulsive interactions in eq. (2.11) the values $E_R(r_0) = 0.501$ eV and $p = 14.6$, which correctly reproduce the lattice constant, bulk modulus and bulk cohesive energy [21] of W. Since the bandwidths of Re and W are nearly the same [22], we assumed the same values for the hopping integrals t_{ReRe}, t_{WRe} and t_{WW}. For these two neighbouring elements in the periodic table, we assumed the same values of $E_R(r_0)$, p, q and U. For the band filling of Re adsorbates the atomic value of 6 electrons has been used.

The W(110) substrate has been considered as unrelaxed and unreconstructed [16]. We have taken into account direct interactions between adsorbates at nearest or second nearest neighbour positions. From our calculation, we found the long-bridge [23] adsorption site of Re atoms (see also fig. 1a) to be most stable. The discrepancy with the work of Desjonquères and Spanjaard [20], who favored a less symmetric adsorption site arises probably from a lower accuracy in their density of states calculation.

In the calculation of band structure and correlation energies the adsorbate and all neighbouring substrate sites have been considered. At each of these sites we calculated the local density of states for the five d-orbitals by using the recursion technique [24]. The continued fractions representing the local densities of states have been terminated after 4 levels by a (moment-conserving) quadratic terminator [25] adjusted to the lower and upper band edge in the bulk. For each adsorption geometry we used substrate clusters of a size which allows calculations of the first 8 moments of the density of states exactly. Such clusters usually consist of several hundred atoms.

The adsorption geometries considered for the "duo" and "trio" interactions are shown in figs. 1a and 2a, respectively. For each adsorbate position, the adsorbate relaxations have been determined by minimizing the total energy of the system. We only considered relaxations perpendicular to the surface which were assumed to be equal at all adsorbate sites.
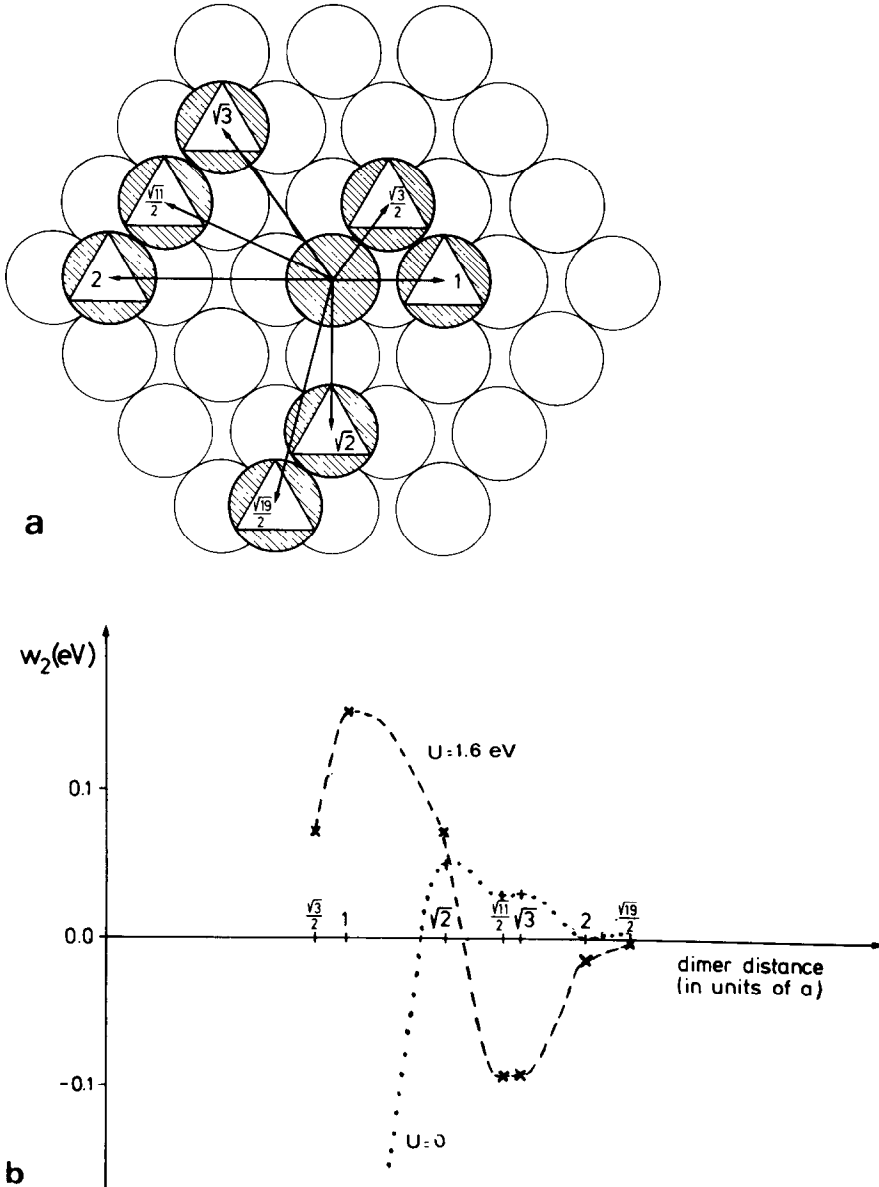
Fig. 1. "Duo" interactions w_2 in $Re_2/W(110)$. (a) Schematic drawing of the adsorption geometry. Substrate W atoms are shown as open circles, Re adsorbates are hatched. (b) Interaction energies w_2 as a function of the mutual adsorbate distance (in units of the substrate lattice constant a). The dashed line connects calculated duo interaction energies for different Re_2 arrangements. For comparison, the dotted line connects data points obtained by neglecting correlation terms.

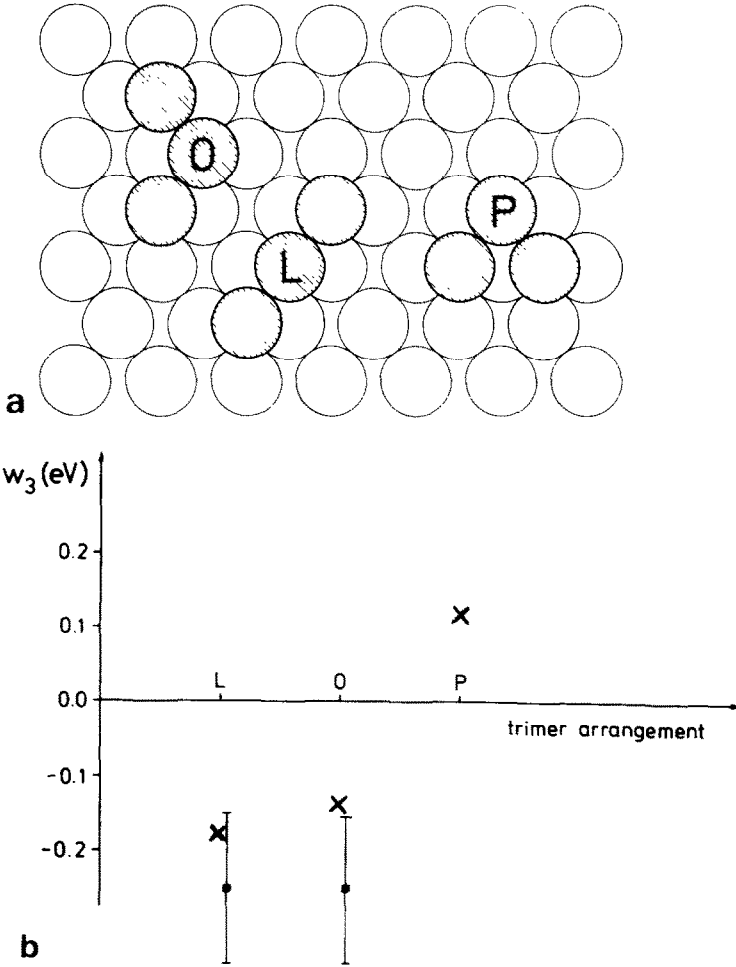Fig. 2. "Trio" interactions w_3 in $Re_3/W(110)$. (a) Adsorption geometry of the linear (L), open (O) and pointed (P) trimer. (b) Corresponding interaction energies (crosses). The experimental data (black squares) are taken from ref. [3].

The results of our calculation for Re_2 in different arrangements are given in fig. 1b and table 1. As can be inferred from the dashed curve which represents interactions obtained by neglecting correlation energies (by setting $U = 0$ in eq. (2.8), the neglect of such terms would suggest a strong "duo" attraction in constrast to the experiment [3].

In fig. 3 we investigated the influence of correlation energies on the nearest neighbour interactions by varying the value of the intra-atomic Coulomb

Table 1
Re "duo" interaction energies w_2 on W(110) as defined in eqs. (2.1) and (2.2), without and with correlation terms. Adsorbate arrangements are shown in fig. 1a

Re$_2$ distance (units of the lattice constant)	w_2 ($U = 0$ eV) (eV)	w_2 ($U = 1.6$ eV) (eV)
$\frac{1}{2}\sqrt{3}$	-1.13	$+0.07$
1	-0.41	$+0.15$
$\sqrt{2}$	$+0.05$	$+0.07$
$\frac{1}{2}\sqrt{11}$	$+0.03$	-0.09
$\sqrt{3}$	$+0.03$	-0.09
2	$+0.00$	-0.01
$\frac{1}{2}\sqrt{19}$	$+0.01$	-0.01

integral U. At each value of U considered we have taken care of changes of $E_R(r_0)$ and p in order to reproduce the correct bulk constants. As can be inferred from this figure, we only can explain the observed repulsive nearest neighbour "duo" interactions by assuming U to exceed a threshold value $U_t = 1.6$ eV [17]. This value has been kept throughout the calculation. The small value of the Coulomb integral U to bulk bandwidth W ratio $U/W < 15\%$ justifies a perturbation theory treatment of correlation energies. As shown in table 1, using $U = 1.6$ eV instead of 0 eV not only changes the sign, but also reduces the interaction energy by one order of magnitude for the nearest neighbour site.
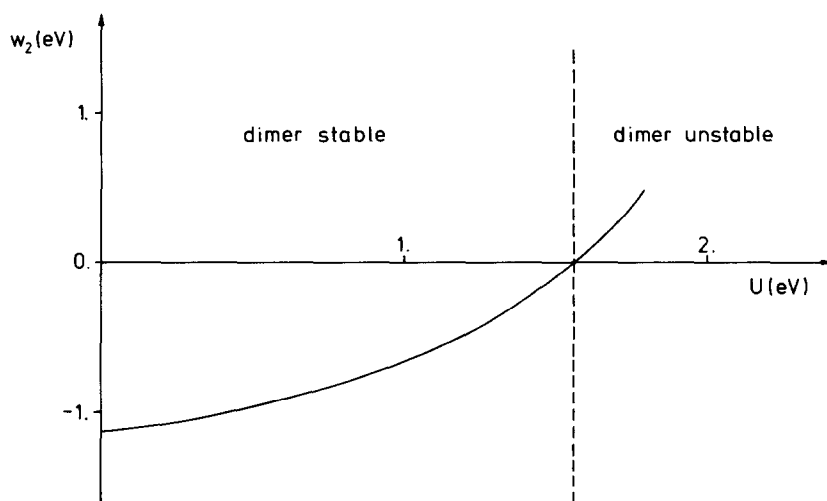

Fig. 3. "Duo" interaction energy in the nearest neighbour Re dimer (given by $d = \frac{1}{2}\sqrt{3}$ in fig. 1 on W(110), as a function of the intra-atomic Coulomb integral U.

In fig. 2b we present results for the "trio" interaction energies in $Re_3/W(110)$. The predicted attractive interactions for the "linear" (L) and "open" (O) trimers agree with the experimental values [3]. The "pointed" (P) trimer which we find to be unstable has not been observed in the experiment [3].

Due to the low symmetry of the problem introducing a large number of free parameters, the self-consistency procedure is more delicate. In eq. (2.14), which determines the adsorbate leves ϵ_i^α, the change in crystal field $\Delta\phi_i^\alpha$ is not known. Therefore we adopted the following procedure. In eq. (2.14) we neglected the orbital dependence of $\Delta\phi_i^\alpha$ and $U_{ii}^{\alpha\beta}$. Further neglecting inter-orbital and interatomic Coulomb interactions as mentioned before, we obtained

$$\epsilon_i = \epsilon_i^0 + \Delta\phi_i + v\Delta\langle n_i \rangle. \tag{3.1}$$

For the L- and the O-trimer the change in the crystal field at the two terminal atoms has been obtained from the nearest-neighbour Re dimer, which is justified by the similar local environment. No such simple determination of $\Delta\phi_i$ is possible at the central atom. We consider the level $\epsilon_A = \epsilon_3$ of the middle adsorbate as the only free parameter which is determined by satisfying the global charge neutrality and eq. (3.1) at both terminal sites. In these trimers the charge at the terminal atoms exceeds that on the middle atom by ≈ 0.1 electrons.

In the P-trimer the crystal field is not known at any Re site. The two inequivalent atomic levels are varied in a way which guarantees global charge neutrality. As in the previously considered trimer arrangements – and essentially independent of the adsorbate level choice – we observed an average charge transfer of ≈ 0.6 electrons from the substrate to the Re trimer. However, only a strong charge transfer of ≈ 0.5 electrons from both "terminal" to the "central" atom makes the pointed trimer unstable. This agrees with the tendency of an increasing charge at the middle atom which accompanies an increasing interaction between the terminal atoms. The instability of the P-trimer is mainly due to the first order correlation effects depending on charge transfer and cannot be explained in models based on local charge neutrality [18].

In the linear Re tetramer on W(110); a similar procedure has been adopted as in the case of L-Re_3 by taking the same value of the crystal field at the terminal atoms as in the nearest neighbour dimer. This tetramer has been found slightly unstable, with an interaction energy $w_4 = +0.04$ eV. This result agrees with the FIM experiments of Fink and Ehrlich [3] who did not observe this tetramer position. Due to the low symmetry of the observed tetramers and pentamers, no attempt has been made to calculate the corresponding interactions.

4. Discussion

From the results presented in the previous section we concluded that for an explanation of the observed "duo" repulsion and "trio" attraction in $Re_n/W(110)$ the correlation terms are necessary. The importance of energy contributions beyond the band structure terms for the understanding of this behaviour also follows from a simple model which is similar to that used in ref. [18]. For simplicity we neglect atomic relaxations and replace pairwise repulsive terms by a hard core repulsion. We assume further the same type of atoms for the adsorbate and metal substrate. We use effective coordination numbers Z_{eff} given, for a bcc structure, by [26]

$$Z_{eff} = Z_1 + 0.4Z_2 + f^2 Z_{ads}. \tag{4.1}$$

Z_1, Z_2 and Z_{ads} are the number of first, second neighbours and, for adsorbates, number of adsorbate neighbours, respectively. f is related to the hopping integral between two adsorbate atoms and can be set to zero in absence of direct interactions. Since in the second moment approximation based on local charge neutrality the binding energy of an atom is proportional to the "local bandwidth" (or square root of the second moment of its local density of states), the total energy can be written as a sum over all sites i as [26]

$$E_{tot} = -\sum_i \sqrt{Z_{eff}(i)/Z_{eff}(bulk)} \; E_{coh}(bulk). \tag{4.2}$$

Using the definition of two- and three-body interactions given in eq. (2.1), the nearest neighbour dimer energy $w_2(nn)$ and the interaction energy of a linear trimer $w_3(L)$ are given by

$$w_2(nn) = -\left(2\sqrt{2.8 + f^2} - 3.35\right) E_{coh}(bulk)/\sqrt{10.4}, \tag{4.3a}$$

$$w_3(L) = -\left(2\sqrt{2.8 + f^2} + \sqrt{2.8 + 2f^2} - 5.04\right) E_{coh}^{(bulk)}/\sqrt{10.4}. \tag{4.3b}$$

We first note that with direct interactions between adsorbates absent ($f = 0$), w_2 and w_3 are equal to zero. Including these interactions ($f = 1$) and using $E_{coh}(bulk) = 8.8$ eV for W yields attractive interactions $w_2(nn) = -1.5$ eV and $w_3(L) = -2.9$ eV. While $w_3(L)$ appears to be much more stable than $w_2(nn)$, both magnitudes are unphysically large and are counteracted by repulsive correlation energies, which result in destabilizing the nearest neighbour Re dimer on W(110).

It should be noted that models based on local charge neutrality, even if they consider correlation energies, neglect such terms arising from the first order perturbation theory. In this way, the P-trimer is predicted as the most stable Re_3 arrangement, in contrast to the experiment.

Correlation energies amount to $\approx 10\%$ of the band structure energy and

play the most important role for a half filled band, which is the case in our system. As shown in our calculation, these terms are most important to describe isolated adsorbed impurities or molecules whose mutual interactions they decrease. In the latter case, as shown in appendix A, only the inclusion of these terms allows one to make quantitative predictions. It is interesting to note that the threshold value $U = 1.6$ eV determined from the "duo" interactions also correctly reproduces dissociation energies of free diatomic transition metal molecules.

As already pointed out by Burke [11] who calculated interactions between two W atoms on W(110), neglecting direct interactions between neighbouring adsorbates (which however lacks physical justification) would automatically lead to a repulsive interaction even in the case where correlation terms are disregarded. It is interesting to note that an artificial reduction by $1/2$ of hopping integrals between adsorbates would lead to repulsive "duo" interactions in absence of correlation terms. In transition metal dimers this unrealistic procedure also would correctly reproduce observed molecular constants. A value of 0.2 eV is found between the level ϵ_1 (one Re atom on W(110)) and ϵ_2 (two nearest neighbours Re atoms on W(110)), the direct interaction Re–Re plays a major rule. It is also the decreasing strength of the direct interaction which makes the next nearest neighbour ($d = 1$) Re_2 interaction more repulsive than that of the nearest neighbour ($d = \frac{1}{2}\sqrt{3}$) dimer.

For the Re dimers beyond the fourth nearest neighbour position, our results shown in fig. 1b suggest an attractive interaction whose magnitude is inferior to the next nearest neighbour repulsion. A similar damped oscillatory behaviour of the interactions has already been suggested in the model work of Grimley [9]. From our calculation we predict an exclusion zone for the existence of a stable Re dimer up to the fourth nearest neighbour site. This is in quantitative disagreement with the results of Fink and Ehrlich [3] who found Re dimers unstable up to the 7th nearest neighbour site. The discrepancy probably arises due to the extreme sensitivity of the first order perturbation theory contribution to E_{corr} in eq. (2.8) to charge transfer. While it is known that our method slightly overestimates charge transfers, these effects are most pronounced for the fourth and fifth nearest neighbour positions where the restrictions due to a limited cluster size considered for the global neutrality and the number of levels used in the continued fraction reduce the reliability of quantitative results.

The importance of adsorbate relaxations on the interaction energies depends on the value of U. For a Re monomer, $U = 0$ eV gives a 9% adsorption bond contraction and a corresponding relaxation energy $\Delta E_{relax} = -0.44$ eV, nearly 10% of the the calculation adsorption energy $E_{ads} = 5.94$ eV. Since the magnitude of relaxations decreases from a single adatom to a trimer, relaxation terms do not cancel completely in eq. (2.1) and modify the interaction energy by $\leq 2\%$ per adatom. Using $U = 1.6$ eV reduces the bond contraction
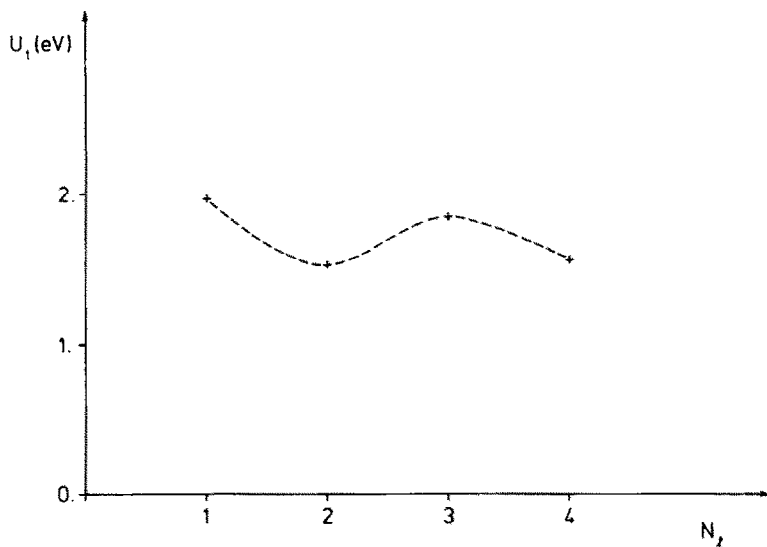
Fig. 4. Threshold value U_t of the intra-atomic Coulomb integral for an unstable nearest neighbour Re dimer on W(110) as a function of the effectively used continued fraction length N_1.

to 2% and the relaxation energy by an order of magnitude, while increasing the adsorption energy to $E_{ads} = 7.8$ eV.

This increase in the heat of adsorption due to the correlation terms improves the agreement with experimental data [20]. Our calculations with $U = 1.6$ eV indicate very similar adsorption bond contractions of 1–2% for Re monomers, dimers and trimers. In contrast to a calculation with $U = 0$, the corresponding relaxation energies nearly cancel in the interactions as defined in eq. (2.1).

The level of accuracy required for our densities of states, i.e. the correct reproduction of its first 8 moments, results in a reasonable range and a damped oscillatory behaviour in the interactions shown in fig. 1b. Clearly, the second moment approximation can only describe interactions between adsorbates in nearest and next nearest positions.

In our calculation the threshold value $U_t = 1.6$ eV for a nearest neighbour Re_2 repulsion has been selected for a number of levels $N_1 = 4$ in the continued fraction expansion of local densities of states. In fig. 4 we investigated the dependence of U_t on N_1 and found a damped oscillatory behaviour which relatively quickly reaches a constant value. It should be noted that U_t mainly depends on charge transfers which, as integrated values, do not depend sensitively on the shape of the density of states.

The results for the "duo" and "trio" interactions in Re adsorbed on W(110) as given in figs. 1 and 2 suggest a strong dependence on the atomic configuration (especially for the trimers). Since the "duo" and "trio" interactions are

also of comparable magnitude, the latter should not be neglected in calculations of adsorbate phase diagrams.

As already mentioned in connection with the $Re_3/W(110)$ calculation, the low symmetry of the problem makes the self-consistency procedure and quantitative predictions of adsorbate interactions difficult in more complex systems. Such an interesting problem are Re interactions on the (anisotropic) W(211) surface. Here, our preliminary results indicated also an anisotropy of "duo" interactions, as observed in the FIM experiment [3].

Experimental investigations of other adsorbates than Re on W(110) showed that in these systems the "duo" interaction is attractive [4,28]. We could speculate that in these systems with nearly full or nearly empty d-band the role of correlation energies inducing the repulsion decreases.

In general, the hybridization between the adsorbate and substrate subsystem weakens the interactions between adsorbed atoms [29]. Clearly, the resulting relative importance of the adsorbate–adsorbate and adsorbate–substrate interactions determine whether the adsorbate prefers a commensurate or incommensurate structure with respect to the substrate. The self-consistent treatment of the adsorption system can play an important role in systems where charge transfer changes the population of bonding or antibonding adsorbate orbitals considerably, thereby modifying the direct interactions within the adsorbed layer.

As has been pointed out previously [18], the value of the intra-atomic Coulomb integral U can be estimated, if the adsorbate interactions are known accurately enough. Within our formalism, it even appears possible to give a lower and an upper limit for U from the knowledge that the dimer, trimer, etc. interactions are attractive or repulsive.

The extension of our formalism to adsorbates of different types is straightforward. The study of interactions between adsorbed CO and O_2 molecules could give insight into the problem of coadsorption phases which determine the surface oxidation reaction. The interactions between adsorbates play an important role not only in catalysis, but also determine the interface formation and the possibility of surface alloying.

In summary, we presented a calculation of interactions between two and more impurities on transition metal surfaces. The total energy of the adsorbate–substrate system was calculated in a self-consistent way within the tight-binding formalism including correlation energies and pairwise interatomic repulsion terms. The inclusion of correlation energies and adsorbate relaxations changed the magnitude of the interatomic interaction but not its oscillatory distance dependence. In the case of Re_2 on W(110) electron correlations have been found essential to explain the observed long-range repulsive force. Also the predicted value for the (attractive) interaction within the linear and open Re trimer showed quantitative agreement with recent experimental data.

Acknowledgements

Appendix A. Calculation of molecular constants

The calculation of molecular constants by using bulk parameters imposes a severe test to our formalism. In the following we apply it to homonuclear clusters and present numerical results for diatomic molecules. The energy of a free cluster is given by

$$E_{tot} = E_{MO} + E_{corr} + E_{rep}. \tag{A.1}$$

Here, the (one-electron) molecular orbital energy E_{MO}, directly obtained from the diagonalization of a finite Hamiltonian in eq. (2.3), replaces the band structure energy of the solid in eq. (2.2). The repulsive energy E_{rep} has been given in eq. (2.10).

Due to the local charge neutrality, similar to the bulk, the first non-vanishing term in the expression for the correlation energy E_{corr} eq. (2.8), arises from the second order perturbation theory and consists of terms inversely proportional to the "local bandwidth" W_i at the site i,

$$E_{corr} \propto \sum_i 1/W_i. \tag{A.2}$$

The "local bandwidth" can be conveniently defined as the square root of the second moment of the local density of states [24],

$$W_i(r) = \sqrt{\sum_{j \neq i} t_{ij}^2(r)}. \tag{A.3}$$

In the second moment approximation, by using the distance dependence of the hopping integrals given by eq. (2.13), the cluster correlation energy can be related to the corresponding bulk values as

$$E_{corr} = E_{corr}(\text{bulk}) \sum_i \frac{\sqrt{Z_{eff}(\text{bulk})}}{\sqrt{\sum_j \exp\left[-2q(r_{ij}/r_0 - 1)\right]}}. \tag{A.4}$$

Here Z_{eff} is the effective coordination number [26] given in bcc metals by

$$Z_{eff} = Z_1 + 0.4Z_2, \tag{A.5}$$

where Z_1 (Z_2) are the numbers of first (second) nearest neighbours.

Since to our knowledge no data exist on W_2 or Re_2 molecules, we apply our formalism to Mo_2. For Mo we use parameters which have been previously found to reproduce bulk properties [20]. The nearest (next nearest) neighbour hopping integrals are $dd\sigma = -1.2729$ eV (-0.7711 eV), $dd\pi = 0.7031$ eV (0.4257 eV) and $dd\delta = 0$ eV (0 eV). The bulk nearest neighbour distance is $r_0 = 2.73$ Å and $E_R(r_0) = 0.712$ eV. The bulk values for the distance dependence of the hopping integrals are $q = 3.5$ and $p = 10.9$, respectively, and for the Coulomb integral we used $U = 1.0$ eV, which yielded a bulk correlation energy $E_{corr}(bulk) = 0.3$ eV.

A calculation of the Mo_2 molecule, with $U = 0$, yielded a shortened (with respect to r_0) bond length $r_e = 2.4$ Å, a dissociation energy $D_e = +5.4$ eV and a vibration frequency $\omega_e = 490$ cm^{-1}. A comparison with the corresponding experimental values [30] ($r_e = 1.93$ Å, $D_e = 4.1 \pm 0.7$ eV and $\omega_e = 477$ cm^{-1}) shows that especially the dissociation energy and the bond length have been overestimated.

A calculation with bulk parameters, which includes correlation terms as given in eq. (A.4), decreases the dissociation energy to $D_e = 4.0$ eV and the bond length to 2.3 Å, but slightly increases the vibration frequency to $\omega_e = 500$ cm^{-1}. The improved agreement with the experiment seems astonishing in view of the rough approximation used for the correlation terms in a diatomic molecule.

It is interesting to note that improved agreement with experiment could also be obtained by neglecting correlation energies and strongly modifying some parameters. Essentially, a reduction by half of the repulsive and hopping terms and slight changes of p and q would also reproduce the correct molecular constants. Such ad-hoc changes of parameters lack, however, physical justification.

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