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## Tight-binding calculations of the electronic structure of small transition-metal clusters on a W(110) surface

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**Abstract.** The electronic structures of small clusters of tungsten and rhodium on a W(110) surface have been calculated within a d-electron tight-binding approximation using the recursion method. The adatom orbital energies and the total energy calculated for three tungsten adatoms on the surface were least for a triangular cluster configuration. For three rhodium adatoms, a linear-chain arrangement gave a lower total adatom orbital energy than that given by a triangular geometry, although the system energy remained higher. The calculations demonstrate the importance of non-bonding electrons for cluster structure and partially account for stabilization of the linear-chain structure for rhodium adatom clusters on a tungsten W(110) surface seen by field ion microscopy.

### 1. Introduction

In studies of the growth of metals on transition-metal surfaces, much has been learned about film structure and epitaxial relationships from LEED and electron microscopy [1, 2]. For metal film growth on close-packed surfaces, however, there is much less information about the nature of the nuclei from which overlayers develop and it is not clear whether nucleation occurs predominantly in steps or by spontaneous cluster formation on terraces. For the latter situation it is commonly supposed that, for transition metals, a cluster of any size will be stable relative to the separated adatoms. Studies at the atomic level with a field ion microscope, however, demonstrate that this is not generally true [3–7].

For the W(110) surface, at least, it is now well established that the strength of the interaction between adatoms is controlled by the electronic structure of the adsorbate. Thus the binding energy of a dimer decreases with increasing occupancy of the adsorbate d-shell from 0.6 eV for Ta<sub>2</sub> to 0.3 eV for W<sub>2</sub> and to near zero for Re<sub>2</sub>. The dimer binding energy remains at or below 0.2 eV for adsorbate metals if the d-shell is more than half full [3]. The interactions are indeed so weak that for adsorbate metals such as Re, Pd and Ir the weak oscillatory interaction at long range due to indirect coupling via the surface can be studied [8–11]. Binding energies of a similar magnitude are also seen for adatoms on the Ir(111) surface [12].

The weak binding of clusters with adsorbate metals with d-shells more than half full is accompanied by a strong tendency for the formation of polyatomic clusters with a

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linear-chain structure. On the W(110) surface, linear clusters of Ir, Pt and Pd adatoms are oriented along the surface  $\langle 111 \rangle$  close-packed directions [4,5]. Similar behaviour is seen for Rh on W(110) and Mo(110) [13], Pd on Ta(110) [6] and for Ir on Ir(100) [7]. Such clusters cannot develop directly into coherent monolayer films and either chain-to-island transformation or nucleation of islands at chain-chain intersections becomes essential for monolayer growth [3-6]. The electronic structure of the adsorbate may thus exert a dominant influence on the nature of the sub-monolayer films and the mechanism for film growth.

In order to understand the nature of these linear-chain structures for clusters of the later transition metals on W(110), electronic structure calculations have been made within a d-electron tight-binding approximation for single adatoms and three-atom clusters of tungsten and rhodium on the W(110) surface. Trimers were chosen as the smallest clusters for which there could be an alternative geometry and for the purposes of correlation with an experimental study of the growth of rhodium films on W(110) [13]. The results clearly demonstrate the important role of non-bonding electrons in the adatom and both confirm and amplify a qualitative discussion of the first field ion microscopic (FIM) observations of cluster structure and stability given by Parsley [14].

## 2. The calculation procedure

The calculation assumes that the systems considered are adequately described by a d-electron tight-binding approximation and is similar to the calculations of the adatom binding energy of dimers on W(110) reported in recent years [15-17]. This assumption is not unreasonable since a number of properties of the transition metals are adequately described within this approximation [18]. Furthermore, since we are comparing similar structures, we have only considered the d-band energy contribution to the total energy. This is clearly a simplification and it will be seen later that for a more complete understanding of adatom clusters it is necessary to perform more elaborate calculations.

The recursion method [18] was used to obtain the local density of states (LDOS) for the d-orbitals of a group of atoms consisting of the adatoms and up to 19 surface atom neighbours embedded in a block of 300 tungsten atoms arranged as a stack of six (110) layers. The calculations were carried out for the clean (110) surface, for the surface with single adatoms of either tungsten or rhodium, and for the surface with either linear or triangular clusters of three tungsten or rhodium adatoms (see figure 1). In all cases the adatoms were placed on the lattice sites so that all inter-atomic distances were taken to be the same as those in the bulk lattice. As a further approximation, relaxation of the lattice around the adatoms was not considered. The hopping parameters for the W-W and Rh-Rh interactions were calculated from the bulk values of these elements while for the W-Rh interaction the parameters were set to the geometric mean of the W-W and Rh-Rh parameters [19]. The atomic d-level and occupancy of the atoms was set at  $-6.2$  eV and five electrons for tungsten and  $-10.42$  eV and eight electrons for rhodium.

To approach a self-consistent charge distribution the orbital d-levels were shifted iteratively until the changes in the atom charges were less than  $0.001e$  while the group of 22 atoms was kept collectively neutral. The computation of the LDOS was restricted to this group, consisting of the adatoms and their immediate neighbours as indicated by the labelled atoms in figure 1. Within this group symmetry permitted a further

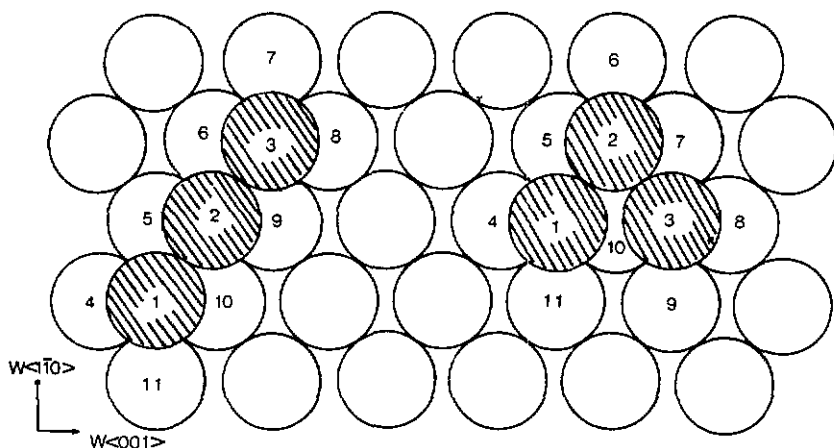


Figure 1. Cluster geometry on the W(110) surface: (a) linear cluster; (b) triangular cluster. The labelled atoms are the adatoms and their neighbours in the first substrate layer. The near neighbours in the second layer are not shown for clarity.

reduction in the number of atoms for which the calculations had to be performed. The d-bond energy for an orbital  $\alpha$  at site  $i$  was calculated as [20, 21]

$$U_b = \int_{-\infty}^{E_f} (E - \epsilon_\alpha^i) n_\alpha^i(E) dE$$

where  $n_\alpha(E)$  is the LDOS of the orbital and  $U_b$  extracts the energy changes arising specifically from the changes in the LDOS broadening and occupancy. In order to demonstrate the changes in the orbital bond energies between different adsorbate cluster configurations, we consider relative bond energies  $U_{br}$ . For example, for a cluster adatom orbital  $\alpha$ , the bond energy relative to the corresponding orbital for a single adatom is

$$U_{br\alpha}^i = U_{b\alpha}^i(\text{cluster}) - U_{b\alpha}^i(\text{single}).$$

These relative orbital-bond energies suffice for examining the source of the differences in stability between the different cluster configurations. However, in order to derive the difference in the d-band energy of the two structures, the energies of the adatoms were considered together with the near-neighbour substrate atoms.

### 3. Results and discussion

#### 3.1. Single adatoms

The level densities for single adatoms, shown for tungsten in figure 2, show pronounced broadening of those adatom levels corresponding to orbitals projecting into the surface. The broadening is smaller for rhodium than for tungsten, as would be expected from the weaker interaction of rhodium with the tungsten surface. However, in both cases the  $d_{yz}$ ,  $d_{zx}$  and  $d_{x^2-y^2}$  orbitals contribute approximately 75% of the total adatom orbital-bond energy. The orbitals in the plane of the surface,  $d_{xy}$  and  $d_{x^2-y^2}$  remain

substantially non-bonding in character with narrow high peaks in the LDOS. The occupancy of these orbitals is higher than for the other orbitals of both tungsten and rhodium. However, it should be noted that the iteration of the calculation places unrealistic charges on the adatoms,  $0.15e$  for tungsten and  $0.8e$  for rhodium. It seems likely that, if the adatoms had been required to remain neutral, the occupancy of these non-bonding levels would have been relatively lower since they are the orbitals with the highest level density at the Fermi level.

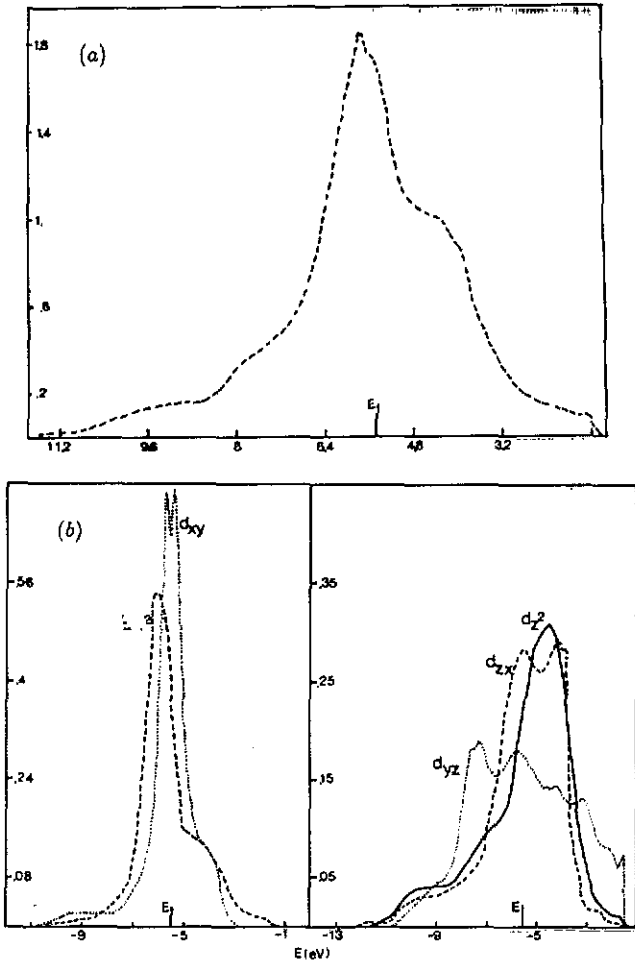


Figure 2. DOS at a single tungsten adatom on the W(110) surface: (a) total DOS; (b) partial DOS.

### 3.2. Tungsten clusters

Bringing three adatoms together to form a cluster broadens the orbital LDOS for both tungsten and rhodium but the consequences of this are rather different and it is convenient to examine the formation of tungsten clusters first. It is necessary only to consider the effect of cluster formation on the adatom orbitals since the orbital

energies of the surface atoms change little. The one exception is the atom beneath the triangular cluster that makes two first-neighbour bonds to the adatoms. It is interesting that the energy change for this atom is close to the energy of its first adatom bond, indicating that the bonding is almost additive. This feature is also seen in the bonding within clusters, even at the level of the individual orbital energies (see table 1).

Table 1. Relative d-bond energies (eV) and electron occupancy (bracketed term) for the adatom orbitals of linear and triangular clusters of tungsten.

Atom	Orbital					Total
	$d_{xy}$	$d_{yz}$	$d_{zx}$	$d_{x^2-y^2}$	$d_{z^2}$	
Linear cluster						
1	-0.6557 (1.088)	-0.1366 (1.079)	-0.2436 (0.936)	-0.4761 (1.098)	-0.2053 (0.919)	-1.7173 (5.121)
2	-1.3035 (1.034)	-0.2593 (1.088)	-0.4757 (0.956)	-0.9703 (0.985)	-0.3491 (1.021)	-3.3579 (5.084)
Triangular cluster						
1	-0.8498 (1.053)	-0.1672 (1.101)	-0.2515 (0.951)	-0.5619 (1.007)	-0.2463 (0.991)	-2.0767 (5.102)
2	-1.4355 (1.12)	-0.2736 (1.088)	-0.5015 (0.917)	-0.8705 (0.952)	-0.5105 (0.983)	-3.5916 (5.06)

The relative contributions of the adatom orbitals given in table 1 show that all orbitals contribute to making both tungsten cluster configurations more stable than separated adatoms. The  $d_{yz}$  and  $d_{zx}$  orbitals make a relatively small contribution associated with the change in the level density from non-bonding to bonding and anti-bonding regions of the orbital DOS (see figure 3). This is to be expected since these orbitals lie in planes perpendicular to the surface and are coupled by  $dd\delta$  overlaps. Both the LDOS and the relative energies show that these orbitals are not significantly affected by the cluster configuration. In contrast, the  $d_{z^2}$  orbitals are more influenced by cluster geometry, although they are also perpendicular to the plane of the cluster and make only a small contribution to bonding. It is worthwhile to note here that in recent cluster calculations of the effect of the DOS of a tungsten tip protusion on scanning tunnelling microscopic (STM) images, the  $d_{z^2}$  orbital is found to be an important active orbital contributing to the tunnelling current [22, 23]. These calculations were done for a small number of tungsten atoms having a (111) structure. Our results appear to show that the  $d_{z^2}$  orbital is sensitive to the configuration of the adatom cluster. Thus, a different structure for the STM tip protusion may be expected to have a  $d_{z^2}$  orbital with a different active role in the STM imaging process.

The difference between the linear and triangular clusters in the  $d_{z^2}$  orbitals arises mainly from atom 2 with two adatom first neighbours. Comparison of the orbital DOS for the two clusters (figure 4) shows that this arises from a transfer of orbital charge from the non-bonding regions of the band for the linear cluster to a strongly bonding peak in the level density for the triangular cluster. The orbital occupancies (table 1) show that there is also some transfer of charge out of  $d_{z^2}$  into the strongly bonding  $d_{xy}$  orbitals that further stabilizes the triangular geometry.

While the contribution of the  $d_{z^2}$  orbital on atom 2 favours the triangular configuration, the  $d_{x^2-y^2}$  orbital on this atom contributes less to the bonding than in the

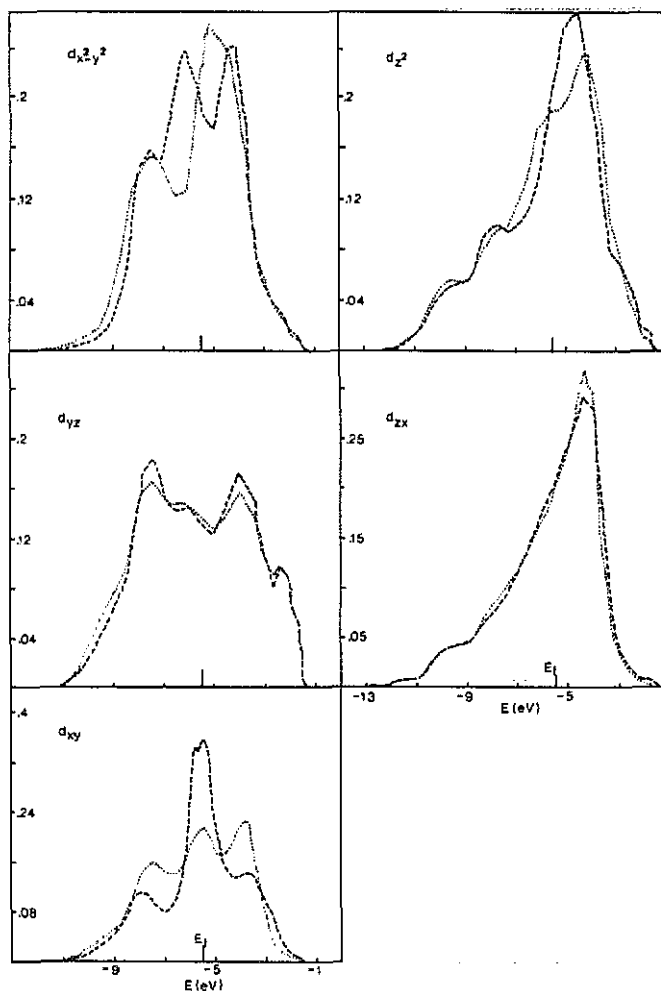


Figure 3. Orbital DOS at atom 1 of the linear (broken curve) and triangular (dotted curve) cluster of tungsten.

linear cluster. The  $d_{x^2-y^2}$  orbitals lie in the plane of the cluster and make an important contribution to its bonding (see table 1). However, the LDOS for this orbital on atom 2 shows that in the triangular cluster it makes a higher contribution to the anti-bonding level density and a lower contribution to the occupied bonding states than in the linear cluster. This effect is partly offset by both bonding and anti-bonding states shifting to lower energy due to the bonding character of the orbital overlaps between the second-neighbour adatoms. Nevertheless, the transfer of the level density to anti-bonding states results in a lower occupancy of the orbital and hence its reduced contribution to the bonding of the triangular cluster.

The effect of the second-neighbour overlap between adatoms 1 and 3 in the triangular cluster can also be seen in the level density for the  $d_{xy}$  orbitals. These orbitals overlap along the bond directions of the cluster and naturally make the largest contribution to the cluster bonding. However, in the triangular cluster, the bonding and anti-bonding regions of the LDOS are shifted to slightly higher energies than those

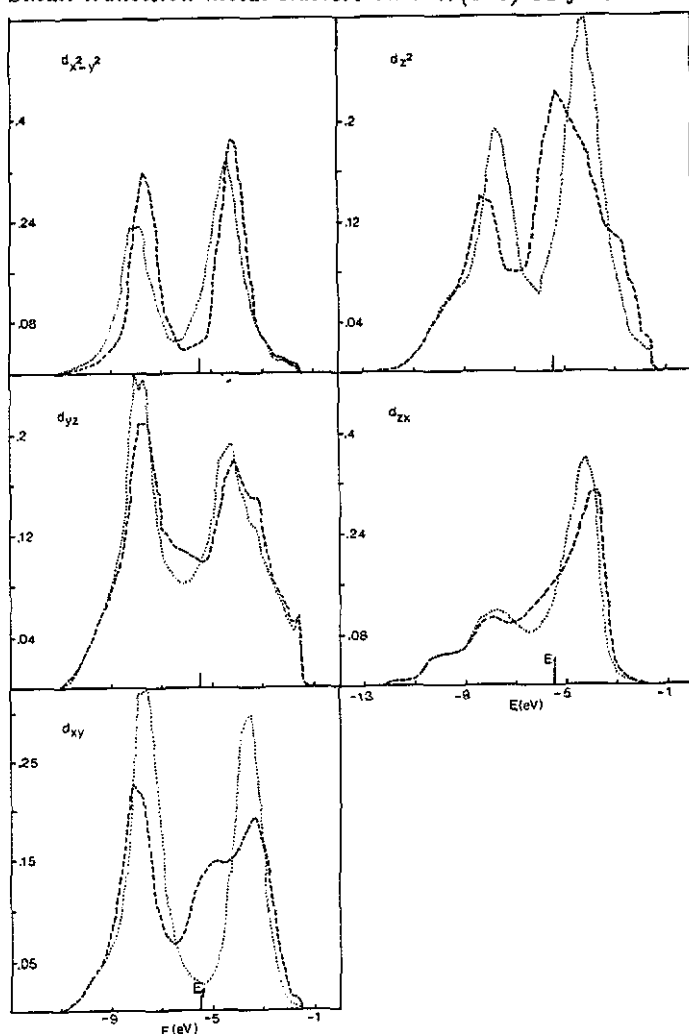


Figure 4. Orbital DOS at adatom 2 of the linear (broken curve) and triangular (dotted curve) cluster of tungsten.

for the linear cluster, due to the unfavourable anti-bonding character of the second-neighbour interaction. This effect is unimportant for the overall cluster bonding, however, and is overwhelmed by the increased bonding level density for the triangular cluster due to the lower non-bonding character of the  $d_{xy}$  orbitals, as compared with these orbitals in the linear cluster. The splitting of both  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals in the terminal atoms of the linear cluster into clear bonding, non-bonding and anti-bonding parts is as expected for the molecular orbitals of a three-atom chain, allowing for some broadening of the states by their interaction with the surface.

### 3.3. Rhodium clusters

For rhodium clusters the relative bond energies of the adatoms are small and indicative of weak bonding (see table 2). The low values compared with tungsten result from the increased orbital occupancy and the reduced width of the adatom level densities associated with the smaller values of the hopping parameters. The differences between



Table 2. Relative d-bond energies (eV) and electron occupancy (bracketed term) for the adatom orbitals of linear and triangular clusters of rhodium.

Atom	Orbital					Total
	$d_{xy}$	$d_{yz}$	$d_{zx}$	$d_{x^2-y^2}$	$d_{z^2}$	
Linear cluster						
1	-0.17 (1.802)	+0.0055 (1.646)	+0.0281 (1.781)	-0.0069 (1.840)	-0.1173 (1.668)	-0.2606 (8.737)
2	-0.3418 (1.723)	+0.0261 (1.666)	+0.0359 (1.795)	+0.0033 (1.847)	-0.1832 (1.663)	-0.4597 (8.694)
Triangular cluster						
1	-0.1508 (1.808)	-0.0215 (1.643)	+0.0312 (1.784)	-0.0189 (1.827)	-0.1265 (1.671)	-0.2865 (8.732)
2	-0.351 (1.703)	+0.0268 (1.667)	+0.0562 (1.805)	+0.0039 (1.848)	-0.1228 (1.680)	-0.3869 (8.701)

the two cluster configurations are also much smaller. Comparison of the adatom energies shows that, whereas adatoms 1 and 3 are slightly more stable in the triangular cluster, adatom 2 is more stable in the linear cluster. The total energy of the adatom orbitals is slightly higher for the triangular cluster, and the linear-chain configuration is thus more favourable for rhodium than for tungsten adatoms.

The origin of the differences between the rhodium cluster configurations can again be seen by comparing the adatoms' LDOS (figures 5 and 6). Since the group orbitals of the three adatom chains are the same as those in the tungsten clusters, the level densities show the same general features. For adatoms 1 and 3 (figure 5), the clear separation between bonding, non-bonding and anti-bonding states seen for tungsten is no longer present due to reduced splitting of the states and this enhances the central non-bonding part of the distribution. Comparison of the orbital DOS of adatom 2 (figure 6) shows that forming the triangular cluster splits the non-bonding states of the linear chain to give well defined bonding and anti-bonding peaks in the level densities for both the  $d_{z^2}$  and the  $d_{xy}$  orbitals. The greater splitting of the  $d_{xy}$  orbital DOS leads to a transfer of charge from the non-bonding region of the  $d_{xy}$  orbital in the linear-chain cluster to the anti-bonding region of the  $d_{z^2}$  orbital at the Fermi level, and consequently a higher energy for the  $d_{z^2}$  orbital in the triangular cluster. It may be noted that charge transfer between these two orbitals also occurs for the tungsten clusters, but in the opposite sense.

In the triangular rhodium cluster, weaker binding of adatom 2 is not compensated for by the slightly lower energy of adatoms 1 and 3 relative to a linear chain. This suggests that the greater stability of the chain cluster for rhodium is mainly associated with electrons on the end atoms in orbitals that are substantially non-bonding.

The total energy obtained by summing the adatom orbital energies is lower for the rhodium linear-chain cluster than for the triangular cluster, apparently in agreement with the observed structure for rhodium. For a proper comparison of the total energies of the two configurations, however, the energies of the substrate atoms must also be included. Unfortunately, the energy for the triangular configuration of a rhodium cluster is then 0.97 eV lower than for the linear chain. Making a similar comparison for a tungsten trimer, the triangular configuration was calculated to be 1.8 eV lower in energy than in a linear chain.

The calculation thus fails to predict the correct stable cluster configuration for

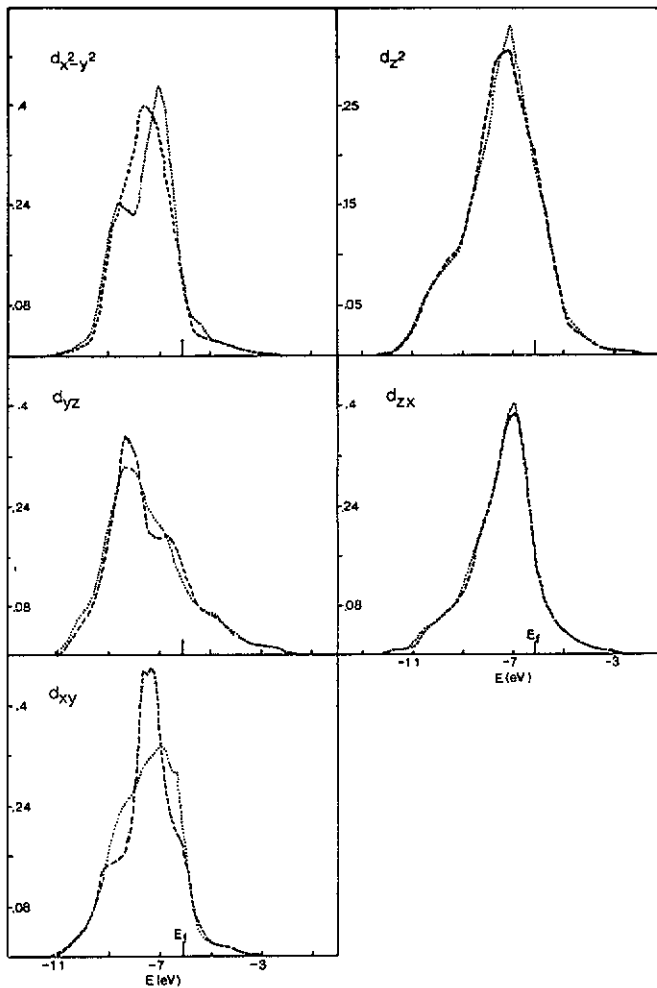


Figure 5. Orbital DOS at adatom 1 of the linear (broken curve) and triangular (dotted curve) cluster of rhodium.

rhodium. We note that other calculations for rhenium trimers [15] also predicted a stable compact structure, contrary to experimental observations. However, our results show a trend in the correct direction towards stabilization of the linear-chain cluster for rhodium, since the energy difference is less than for the triangular trimer. It is notable that the stabilization of the triangular cluster in the calculation comes almost entirely from the energy changes in the substrate atoms accompanying the formation of the more compact cluster. This emphasizes the need to include substrate relaxation in any more detailed calculations. It has been shown recently that substrate relaxation is important for the structure of small clusters on platinum (100) [24] but we believe it to be of secondary importance compared with the adsorbate electron configuration.

The choice between different cluster configurations for rhodium appears to be quite delicately balanced. It is possible that the linear cluster could be further stabilized by electronic correlations and reduced core-core repulsions, which we have not taken into account. Further calculations are clearly needed to examine these points and

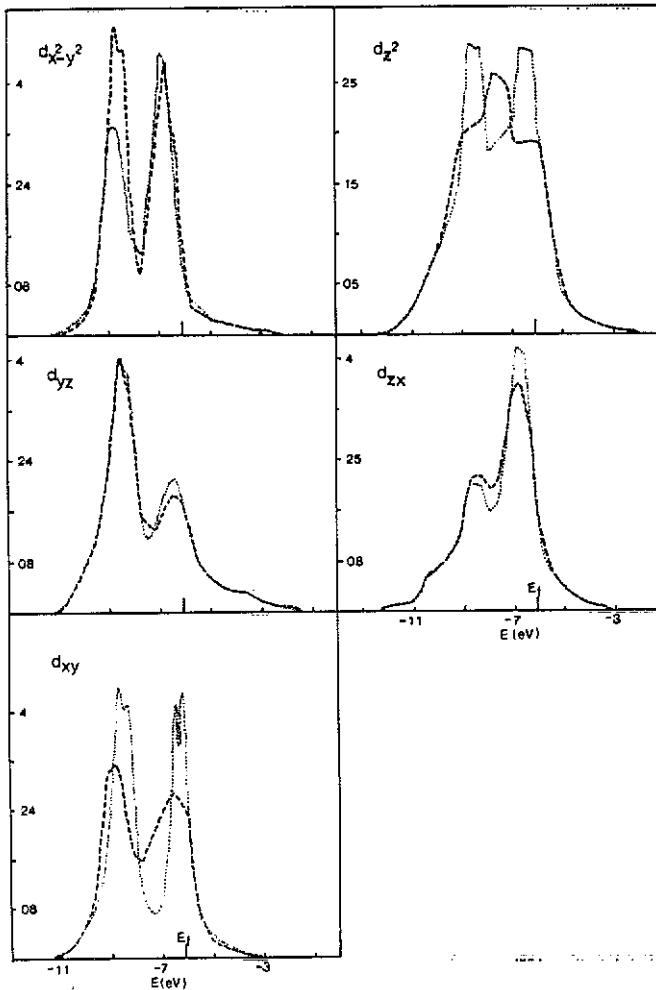


Figure 6. Orbital DOS at adatom 2 of the linear (broken curve) and triangular (dotted curve) cluster of rhodium.

the contributions of *s* and *p* electrons to the cluster bonding. Other calculations [16, 17] indicate that electron correlation effects and magnetism significantly influence the interaction energies between 5*d* metal adatoms in dimers and the stability of adatom clusters on the W(110) surface.

#### 4. Conclusions

Electronic structure calculations have been performed within a *d*-electron tight-binding approximation to examine the LDOS of adatoms of tungsten and rhodium on W(110). The calculations were performed for a three-adatom cluster in a linear chain and a more compact triangular configuration in order to understand the linear-chain clusters seen experimentally for rhodium on W(110). The crucial factor stabilizing the linear-chain cluster for rhodium appears to be the behaviour of the non-bonding orbitals on formation of the cluster, although core-core repulsions and

electron correlations probably also play an important part. The greater non-bonding character of the LDOS for the linear cluster compared with the compact triangular cluster stabilizes the linear form. Examination of the d-bond energies of the adatoms and their near-neighbour substrate atoms shows that the triangular form is lower in energy than the linear cluster for both tungsten and rhodium. However the difference is much less for rhodium than for tungsten, thus showing a trend toward stabilization of the linear-chain cluster for rhodium.

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