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An embedding scheme for calculating charge transfer between adsorbates and metal substrates

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Abstract. A semi-empirical embedded-cluster scheme useful for the study of adsorption on metal surfaces, especially charge transfer between adsorbates and substrates, is presented. To avoid the incorrect description of the high-lying antibonding s and p states of metals by the usual cluster calculation, free-electron-like states bounded in the normal direction are introduced in the basis function to describe the s and p states of the transition- or noble-metal substrate, while the d state is represented in the tight-binding approximation. In addition, effects from the dangling d bonds at the boundary are removed by a projection technique. Such a treatment is able to give a reliable local electronic structure of adsorption systems. Application of this scheme to Cs/W (100) and Cs/Cu (100) shows that the calculated results are in close agreement with those by a first-principles linearised augmented plane waves method.

1. Introduction

There have been a number of theoretical techniques for studying electronic structure and chemisorption properties of solid surfaces. Two models generally used to simulate the surface system are the cluster and slab models (or semi-infinite solid). Of these, the cluster model is especially useful in treating local systems with lower spatial symmetry, such as adsorption, impurity effect, etc. Combined with the theory of quantum chemistry, this model is able to give interpretations and predictions for various properties qualitatively, or in some cases even quantitatively [1]. There is an 'intrinsic' problem, however, associated with the cluster model, since its finite size and free boundary obviously differ from reality. Some properties calculated by the cluster model, e.g. the binding energy of adsorbates, do not show good convergence with increase of the cluster size and sometimes may even lead to unphysical conclusions [2, 3].

This problem arises from the fact that the free-electron band of the metal substrate is not properly described by a cluster in the local configuration. Figure 1 shows a typical spectrum for a Ni₆ cluster quoted from a DV X α calculation [4] and the corresponding nickel crystal bands. Because of their tight-binding character, the d bands are properly reproduced by the densely packed states of the six-atom cluster. On the contrary, the distribution of s states differs greatly from the free-electron band of the crystal. Unlike the dispersive s band of the crystal, there are only two antibonding orbitals (s_u) at the top of the spectrum above the Fermi level from the cluster calculation. These antibonding

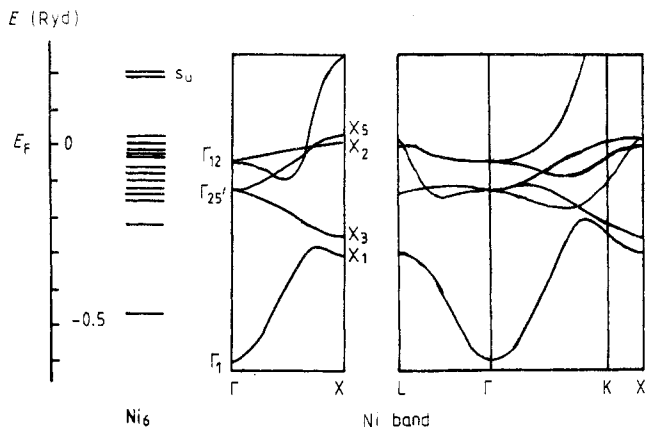


Figure 1. Comparison of the energy levels of a Ni_6 cluster with the energy band of the bulk Ni crystal.

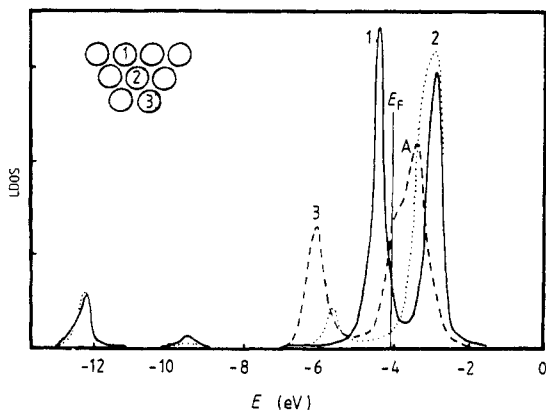


Figure 2. Local density of states of s orbitals for atoms on the surface (full curve), at the boundary (broken curve) and in the centre (dotted curve) of a Cu_{22} cluster. Peak A shows the antibonding peak of the boundary atoms, which is lower than that of the others.

states have the highest energy and their wavefunctions spread mainly in the outer space of the cluster. Therefore, they will exhibit the strongest interaction with alkali-metal adsorbates, whose valence level is just located near them. When simulating a metal surface by a small cluster in a chemisorption study, the difference between these s_u states in the cluster levels and the real surface electron band is expected to give rise to serious problems in the discussion of charge transfer between alkali-metal adsorbate and transition-metal surface. This problem is more prominent on noble-metal substrates, because their d band is fully occupied and the description of the s band structure becomes even more crucial to the charge transfer.

To illustrate this problem more clearly, the partial local density of states (LDOS), calculated by a parametrised LCAO (linear combination of atomic orbitals) approach, for the s orbital of three atoms in a Cu_{22} cluster is plotted in figure 2. Owing to lower coordination, the antibonding peak just above the Fermi level for the boundary atom (peak A of curve 3) lies lower than those of bulk-like atoms (curve 2) and surface atoms (curve 1). When a Cs atom is put on the surface, transferred electrons from the Cs adsorbate will, according to this kind of calculation, first occupy these states even though

the boundary atoms are located far away from the adsorbate on the surface and there is no interaction between them. Therefore, the electron of Cs is transferred to the s orbitals of the Cu atoms at the cluster boundary, which is obviously wrong in the physics of a real system. It should be emphasised that this problem could not be eliminated by increasing the size of the cluster. In fact, calculated charge transfer does not show convergence with increasing cluster size, because more antibonding states will be created as the size increases. The fact that the s band of the substrate is not properly described by a finite cluster has made the calculation unphysical. In a self-consistent calculation, this problem will not be as prominent as in the non-self-consistent one, but it still exists to some extent.

In order to take into account the interactions between a finite cluster and its remaining environment in a real system, several models [5–8] to embed a cluster into an effective medium (e.g. larger cluster [5, 6], Bethe lattice [7] or jellium [8]) have been put forward in the past few years. The earliest attempt was made by Grimley and Pisani [5] when they applied the atomic Hartree–Fock program to a chemisorption system. Using the Dyson equation approach, these authors performed a self-consistent calculation over a small cluster and represented the Greenian operator of the remaining host in the tight-binding approximation. This idea is indeed inspiring, but it can hardly be generalised to any practical system because of the tedious computation work required by a Hartree–Fock calculation. Recently, Kunz [6] derived systematically a series of corrections to energy levels and wavefunctions when the cluster was embedded into a lattice system. In this treatment, interaction with the environment is represented by an external potential (i.e. crystal field). This model gives the perturbative corrections to the antibonding s orbitals, but is still far from the dispersive free-electron band of a real crystal surface. In a quite different way, Muscat embedded the cluster into an electron gas using a multiple-scattering formalism [8]. The potential in the muffin-tin region of the substrate was taken as that of the free atoms, while an empirical screened potential was adopted to describe the adatoms (hydrogen). The calculated results (i.e. adsorbate-induced density of states and binding energy) were in good agreement with that of the first-principles method. This scheme gives a proper description for both the s and d electrons of the substrate. Generalisation of this method to treat ionic and strong covalent bonds at the surface has to avoid the complication of representing the surface Green function and remove the uncertainty in the determination of adsorbate potential. Another similar embedding idea has been used separately by two groups [9, 10] in chemisorption studies, using an overcomplete basis consisting of a few local orbitals and the metal wavefunctions; the adsorbate-induced DOS and binding energy are calculated either by the Green function technique [9] or by the variational scheme [10]. This mixed-basis approach does, to some extent, take into account the interaction between the local orbital and the metal wavefunction. The subsidiary condition that warrants the expansion of the wavefunction as far as possible on the local orbitals suppresses the interaction between the delocalised electron states of metal and adsorbate due to the over-completeness of the basis function.

Similar to the basic idea of Muscat, we present in this paper a modified semi-empirical calculation scheme that is designed to study the charge transfer between adsorbates and metal substrates. In this scheme, s and p electrons of the substrate are described by the plane-wave basis instead of the local atomic orbitals used in the usual cluster calculation. This partly eliminates the boundary problem in a free-cluster simulation. The adsorbate and d state of the substrate are still represented by an appropriate cluster in the tight-binding approximation as in the usual treatment. In addition, in order to remove the effect of dangling d bonds at the cluster boundary, electron population analysis is made

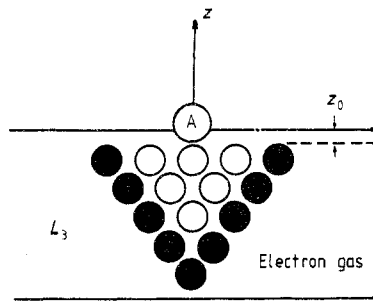


Figure 3. Schematic structure of the embedding cluster, $A/M_m/M_n$: (○) centre cluster including adsorbate A and nearby substrate atoms (M_m); (●) boundary shell (M_n).

only for a small region near the adsorbate by a projection technique. This scheme is basically a cluster approach and therefore retains the simple and efficient character of the cluster model in coping with complex systems that can hardly be treated by a band approach, which is the ultimate goal of this work.

In the present semi-empirical treatment, all the Hamiltonian matrix elements are determined from parameters of inter-atomic interaction and metal pseudopotential given by Harrison [11, 12], together with the experimental data of work function and ionisation energy. This makes the calculation very simple. Although no self-consistency is made, it does provide a reliable physical insight into the interactions between adsorbates and substrates in adsorption systems. The calculated charge transfer for Cs/W(100) and Cs/Cu(100) shows semi-quantitative agreement with the first-principles LAPW results. The method is formulated in detail in section 2, then applied to two systems, and some results and discussions are given in section 3.

2. Method

From the above analysis, it is clear that the free-electron band of the metal substrate cannot be reproduced correctly by the local atomic orbitals of a finite cluster. In the present treatment it is described by bounded plane waves [13] instead of local orbitals. The orbitals of the adsorbate and the d states of the cluster representing the substrate are still represented by atomic orbitals, as usual. In addition, the substrate atoms with d orbitals are labelled by two parts, a centre cluster consisting of the adsorbate (A) and m substrate atoms (M_m) near the adsorbate and a shell of n atoms surrounding the centre cluster (boundary shell, M_n). This is shown schematically in figure 3. In our notation, the whole cluster is expressed as $A/M_m/M_n$. Such a description of metal electron states is closer to that of the real system for both free-electron-like s and p and local d electrons than the usual cluster approach, especially in the region of the centre cluster. The boundary shell surrounding the centre cluster is introduced to ensure that each atom in the centre cluster is situated in an environment with very close similarity to that of a real crystal.

The variational wavefunction for this system is constructed in a mixed basis as

$$|\psi\rangle = \sum_{im} C_{im} |im\rangle + \sum_k C_k |k\rangle + \sum_a C_a |a\rangle \quad (1)$$

where $|im\rangle$ is the m th d orbital at site i of the substrate, $|a\rangle$ is the orbital of the adsorbate and $|k\rangle$ is the plane wave bounded in the infinite barrier [13]. More specifically, the following two real plane waves are used in the basis:

$$\begin{aligned} |k, 1\rangle &= (2/\sqrt{V}) \cos(k_1x + k_2y) \sin(k_3z) \\ |k, 2\rangle &= (2/\sqrt{V}) \sin(k_1x + k_2y) \sin(k_3z) \end{aligned} \quad -L_3 < z < 0 \quad (2)$$

where L_3 is the thickness of the electron gas, $V = L_1L_2L_3$, and L_1 and L_2 are the

renormalisation lengths in the x and y directions, respectively. The wavevectors (k_1, k_2, k_3) are selected to satisfy periodic boundary conditions. Physically, L_1, L_2 and L_3 should be infinitely large, which is of course impossible for a practical calculation. The values used in the present calculation are $L_1 = 6a, L_2 = 6b$ and $L_3 = 5c$, where a and b are the surface primitive translational vectors and c is the nearest layer distance in the normal direction. This means that plane wavefunctions of 30 \mathbf{k} -points (six in the one-eighth irreducible surface Brillouin zone and five in k_3) are used in the basis set. In equation (2), the z axis is chosen perpendicular to the surface and the origin is placed at the position of the infinite barrier, which is about a decay length, $z_0 = -3\pi/8K_F = -0.618r_s$, outside the edge of the surface atomic plane [14] (see also figure 3). For metals, z_0 is between 1.0 and 2.0 au. The infinite-barrier model is an approximate description of the surface electron states, in particular in the sense that the exponential decay of the substrate electrons into the vacuum region outside a decay length has been neglected. However, the interaction between the adsorbate and the substrate, and thus the adsorbate-induced properties, are found to depend less sensitively on the position of the distance (z_0) in the appropriate range (1–2 au). Results of a test calculation are given in the last paragraph of this section.

In the present treatment, all the overlap integrals are neglected for simplicity and the Hamiltonian matrix elements in the secular equation

$$H|\psi\rangle = ES|\psi\rangle \quad (3)$$

are chosen in a semi-empirical way based on Harrison's analysis (see the appendix). Such a choice of the matrix elements seems to be fairly rough compared with more accurate evaluation. However, what we want to show is that these approximations are relatively unimportant compared with the most serious problem in the description of free electrons in the usual cluster calculation. Of course, it is recommended to evaluate these matrix elements exactly and remove other relevant approximations when accuracy in the numerical results is needed.

The calculated eigenenergies and wavefunctions are projected into the centre cluster to give a local partial-wave density of states $\rho_{i\alpha}(E)$. For the s orbital of the substrate atoms, the LDOS is obtained by summing up all the plane-wave components projected into a unit cell (Ω) around an atomic site, i.e.

$$\rho_{js}(E) = \sum_i \sum_{\mathbf{k}} C_{ik}^2 \int_{\Omega} d\mathbf{r} \langle \mathbf{k} | \mathbf{k} \rangle \frac{\sigma}{\pi (E - E_i)^2 + \sigma^2} \quad (4)$$

where a Lorentzian factor is used to broaden ($\sigma = 0.15$ eV) the cluster levels, and i sums over all eigenstates. The Fermi level is determined by requiring charge neutrality of the centre cluster:

$$N = \int_{-\infty}^{E_F} \rho(E) dE = \sum_{i\alpha} \int_{-\infty}^{E_F} \rho_{i\alpha}(E) dE \quad (5)$$

where N is the total number of valence electrons of the centre cluster. The electron population on orbital α of atom i is given by

$$n_{i\alpha} = \int_{-\infty}^{E_F} dE \rho_{i\alpha}(E). \quad (6)$$

The adsorbate-induced dipole moment for a chemisorption system is obtained approximately by summing up the product of charge transfer ΔQ_i and its corresponding z coordinates for each atom in the centre cluster, i.e.

$$P_0 = 2 \sum_i \Delta Q_i \times z_i. \quad (7)$$

The factor 2 comes from the image effect of a metal surface.

Table 1. Calculated properties of a Cs/Cu₉ cluster for different choices of the edge of the surface plane z_0 . The values in parentheses are charge transfers upon Cs adsorption.

z_0 (au)	Integrated LDOS of a unit cell		Population of free electrons		Total charge transfer, ΔQ
	1st layer	2nd layer	1st layer	2nd layer	
0.5	0.90	0.98	1.21 (0.02)	1.47 (0.01)	(0.13)
1.0	1.03	0.99	1.34 (0.04)	1.38 (0.03)	(0.43)
1.5	1.16	0.99	1.43 (0.03)	1.29 (0.03)	(0.45)
2.0	1.31	0.99	1.52 (0.02)	1.21 (0.03)	(0.48)

It should be noted that although the atoms of the boundary shell are not involved in the charge population analysis in this procedure, they do provide an extra electron self-energy (i.e. embedding self-energy) to the electrons in the centre cluster and therefore affect the energy spectrum. This is essential for a good description of the d states of the centre cluster. In the tight-binding approximation, it can be shown that the second-order moment of the density of states is not affected by the atoms beyond the nearest neighbours [5]. This provides us with the basis for constructing the boundary shell, that only the nearest neighbours of the centre cluster need to be taken into account, so this does not sacrifice computing efficiency very much. It should also be noted that the charge neutrality condition of the centre cluster is equivalent to an assumption that charge transfer only occurs between atoms in the centre cluster. This is reasonable due to the small screening length of metals.

To illustrate how the calculated properties of the chemisorption systems depend on the choice of parameter z_0 , results calculated for a Cs/Cu₉ cluster (without boundary shell) are given in table 1 for several choices of z_0 value. In all cases, electron states in the vacuum (i.e. outside the edge of the first atomic layer) are attributed to the atoms of the first layer. It is shown in table 1 that the integrated local density of states and thus the electron population for the s orbital of the first layer atom increase gradually as z_0 increases. The charge transfer, however, changes less sensitively when z_0 varies from 1.0 to 2.0 au, which shows that the infinite-barrier approximation of the free-electron states is acceptable in studying these surface properties.

3. Results and discussion

As a first check of this scheme, we show the calculated electronic structure of a Ni₆ cluster by three different models (i.e. Ni₆, Ni/Ni₅ and Ni/Ni₅/Ni₁₂). Comparison of the local density of states for the three systems is given in figure 4. It is easily seen that figure 4(a) obtained by the usual atomic-orbital cluster method is actually a reproduction of the left part of figure 1. In addition to the incorrect antibonding peaks of s_u states, the calculated d band width (3.0 eV) is narrower compared with the d band (3.78 eV) of a nickel crystal [15]. In figure 4(b), the antibonding peaks disappear and the dispersive free-electron band becomes prominent when the plane waves are introduced in the basis as described in the previous section. However, the narrow d band structure still remains.

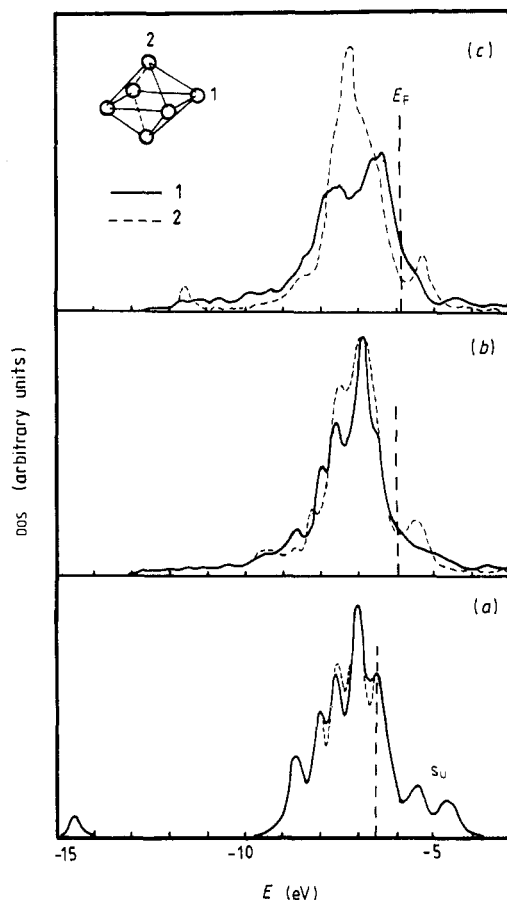


Figure 4. LDOS for two Ni atoms calculated by (a) Ni₆ cluster with atomic orbitals, (b) Ni/Ni₅ and (c) Ni/Ni₅/Ni₁₂.

It does not change until a boundary shell of 12 atoms is introduced as in figure 4(c). This indicates that the present scheme can give a correct description of both s and d electron states of the metal substrate. Plane-wave basis, boundary shell and local projection are three indispensable ingredients to give this rather satisfactory description.

As another check of the method, we applied this scheme to a clean W(100) surface. The calculated LDOS by a W₃₈ (without adsorbate and boundary shell) cluster for the atoms at the surface and in the centre (bulk character) are given in figure 5. It is shown that there are abundant partially occupied surface states in the d band region. The richest one peaks at about 0.3 eV below the Fermi energy and has d₂₂ orbital symmetry. These results are in good agreement with the experimental measurements [16] and other accurate theoretical calculations [17]. Furthermore, other properties that characterise the band structure (i.e. the d band width, the position of the Fermi level, etc) also show agreement with those given by the first-principles method [17].

The main purpose of developing this embedding scheme is to deal with the more complicated chemisorption systems. As a first application, we have performed this embedding calculation on three clusters, Cs/M/M₈, Cs/M₅/M₁₃ and Cs/M₁₀/M₂₈ (M denotes Cu and W), to simulate Cs adsorption on the Cu(100) and W(100) surfaces. The Cs/W(100) system has been studied in detail both experimentally [18] and theoretically [19, 20]. It is widely known that decrease in the work function of the W surface upon adsorption of Cs is due to charge transfer from Cs to the W substrate. Recent photoemission measurements [18] showed that surface states of the substrate play an essential

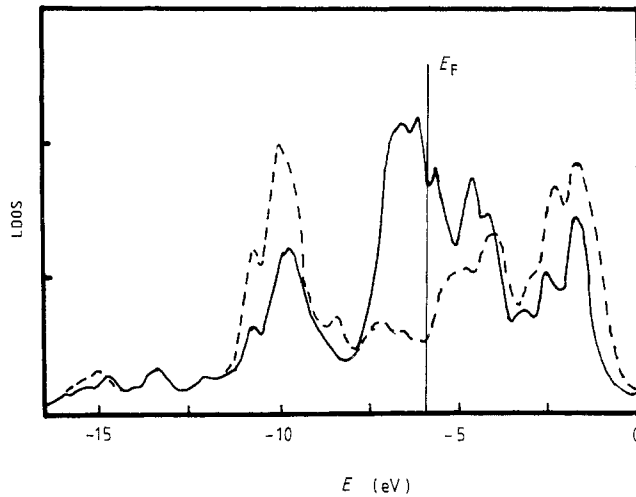


Figure 5. Comparison of calculated LDOS for a W atom at a (100) surface (full curve) and in the centre (broken curve) in a W_{38} cluster.

Table 2. Charge transfers (ΔQ) calculated by Cs/M/ M_8 cluster.

Centre cluster	Cs (6s)	M						P_0 (D)
		d_{z^2}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{xy}	s	
CsW	-0.67	0.24	0.15	0.15	0.07	0.04	0.02	7.39
CsCu	-0.15	-0.01	0.01	0.01	0.01	0.01	0.12	1.51

role in the interaction and charge transfer between the Cs adsorbate and the W substrate. This is further justified by the first-principles theoretical calculations [19, 20]. There is no experimental measurement for the Cs/Cu(100) system. Very recently, the LAPW calculation has been performed on the jellium/Cu(100) system to simulate Cs adsorption on the Cu(100) surface [21]. Much less charge transfer is found for Cs on Cu(100) than on W(100). The interaction picture is also quite different.

In the present calculation, the Cs atom is assumed to sit at a top site. Adsorption height (5.5 au for Cs/Cu and 6.0 au for Cs/W) is estimated presumably from the average of the ionic and covalent radii of the two components, because there is no explicit experimental data about the adsorption geometry in the literature for the two systems. It is found, however, that charge transfer does not exhibit a sensitive dependence on the adsorption site and adsorption height; for example, the total charge transfer for Cs/W(100) increases by about 0.04 when the Cs adsorption height varies from 6.0 to 6.5 au.

Results of the embedding calculation by a Cs/M/ M_8 cluster are given in table 2. For a Cs/W/ W_8 cluster about 0.67 electron is transferred from Cs to W substrate. This is the result mainly of the filling of the d_{z^2} surface band (0.24 electron) of W(100) in accordance with other theoretical calculations [19, 20]. Next to the d_{z^2} state, about 0.15 electron is transferred to the d_{xz} and d_{yz} orbitals. For a Cs/Cu/ Cu_8 cluster, however, much less electron (0.15) is lost from the Cs atom and the transferred electrons are populated mainly on the Cu s orbital, which coincides well with the first-principles calculation [21]. The difference in the results for the two systems arises from the fact that there are

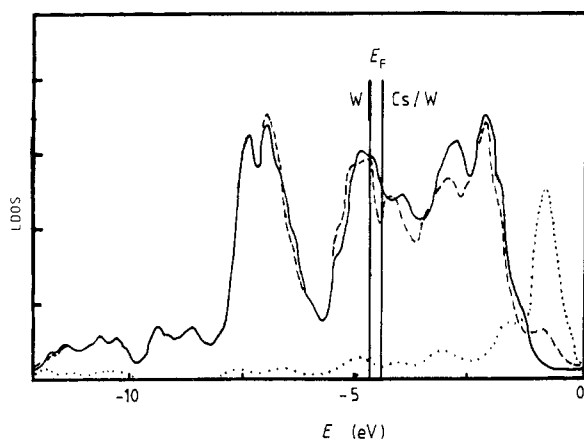


Figure 6. Calculated LDOS of W on a clean (100) surface (full curve), of W on a Cs adsorbed surface (broken curve) and of adsorbed Cs atom (dotted curve), in a Cs/W/W₈ cluster.

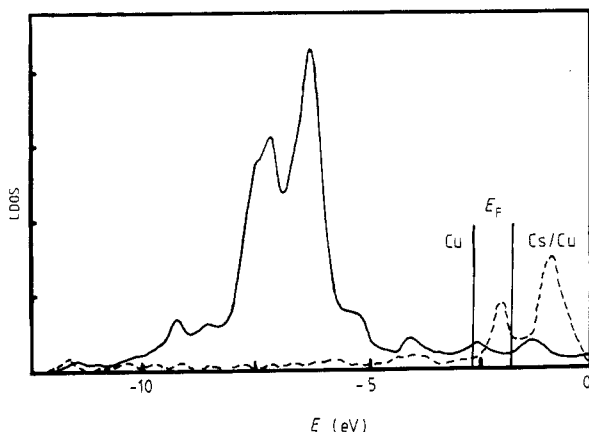


Figure 7. Calculated LDOS of a Cu atom at a (100) surface (full curve) and a Cs atom (broken curve), in a Cs/Cu/Cu₈ cluster. Adsorbate-induced changes are not discernible for the Cu atom in this curve.

abundant localised surface states (figures 5 and 6) near the Fermi level on W(100), while no such prominent surface state exists on the Cu(100) surface (figure 7). It is also shown in table 2 that a perceptible fraction of electrons in the d_{z^2} state of Cu is lost during adsorption, in contrast to the Cs/W(100) system, because a few antibonding states between Cs and the d_{z^2} orbital of Cu lie above the Fermi level while the d band of a clean Cu(100) surface is fully occupied. In addition, the calculated dipole moment (7.39 D) for Cs/W(100) agrees quite well with the experimental initial dipole moment value (7.95–9.05 D) [20] and other theoretical calculations [20, 22, 23]. Also in this calculation, about 0.4 eV shift (with respect to E_F) of the d_{z^2} surface states is found for the Cs/W system as shown in figure 6. This adsorbate-induced shift is in good agreement with the experimental measurement [18] of 0.3–1.0 eV for Cs on W(100) within one monolayer coverage and with the results of the first-principles calculation [19, 20]. These results show that the present scheme can give a semi-quantitative description for the

Table 3. Charge transfers (ΔQ) in Cs/W(100) systems calculated by different clusters. The atoms in the same parentheses are equivalent in space.

Cluster	Cs	W 1st layer		2nd layer (6, 7, 8, 9)	3rd layer (10)	P_0 (D)
		(1), (2, 3, 4, 5)				
Cs/W/W ₈	-0.67	0.67				7.39
Cs/W ₅ /W ₂₁	-0.70	0.28	0.42			7.72
Cs/W ₁₀ /W ₂₈	-0.70	0.20	0.43	0.14	0.03	8.04

Table 4. Charge transfers (ΔQ) in Cs/Cu(100) systems calculated by different clusters. The atoms in the same parentheses are equivalent in space.

Cluster	Cs	Cu 1st layer		2nd layer (6, 7, 8, 9)	3rd layer (10)	P_0 (D)
		(1), (2, 3, 4, 5)				
Cs/Cu/Cu ₈	-0.15	0.15				1.52
Cs/Cu ₅ /Cu ₂₁	-0.39	0.06	0.27			3.89
Cs/Cu ₁₀ /Cu ₂₈	-0.38	0.04	0.16	0.16	0.03	5.80

interaction and charge transfer of chemisorption on metal surfaces. At present, direct comparison with experimental data cannot be made for Cs/Cu(100).

To probe the convergence of charge transfer with cluster size, the results of three clusters for Cs/W(100) and Cs/Cu(100) are listed in tables 3 and 4, respectively. As shown in table 3, for Cs/W(100), the total charge transfer and dipole moment do not change sensitively with cluster size when the number of W atoms varies from 9 to 38, which shows that rapid convergence has been obtained by the present embedding scheme. For the Cs/Cu(100) system, convergence for charge transfer is also achieved on the two larger clusters (Cs/Cu₅/Cu₁₃ and Cs/Cu₁₀/Cu₂₈); however, the dipole moment does not show good convergence with cluster size. This results from the fact that charge transfer on the Cu(100) substrate is not localised on the surface atoms as in the case of W(100). Owing to the relatively longer screening length of the noble-metal substrate, the calculated dipole moment would be lower than that in reality if the cluster size used in the calculation is too small. In addition, the non-self-consistent treatment in this calculation may also contribute more or less to the slow convergence of dipole moment for Cs on noble metals, because several important factors, such as surface potential, electronic screening and on-site energy levels of the adsorbate, are not taken into account in the present calculation.

Nevertheless this does not affect our basic conclusion. From the above calculations, it is found that, by adopting the plane-wave basis for the s and p electrons, a suitable boundary shell and a projection technique, a very good description is obtained for the dispersive surface s and p bands, the local d band width and the local surface states of a clean transition-metal surface. For adsorption systems, a centre cluster with only two atoms may provide a lot of valuable information. The total charge transfer and the physical interaction picture are given for alkali-metal adsorption systems. The calculated charge transfer converges very rapidly with cluster size by the present scheme. All the results show the validity of this scheme for the study of adsorption problems. Although self-consistency is not made in the present calculation, it can be easily adopted to this treatment. As the calculation is straightforward, it is expected to find application to more complex and practical systems.

Acknowledgments

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Appendix. Determination of the Hamiltonian matrix elements

In this calculation, all the matrix elements of the Hamiltonian are determined from empirical parameters: the inter-atomic hopping integrals between local atomic orbitals are taken from the 'solid-state table' in Harrison's book [11]. The hybridisation between d states and free electrons $\langle k|H|d\rangle$ is also given in the same table and [12]. All the parameters (r_d , r_0 , $\eta_{ll'm}$, etc) are obtained from fitting the energy band of bulk materials. The matrix element between an adsorbate orbital and the plane waves is derived as follows:

$$H_{ak} = \frac{1}{2}(H_{aa} + H_{kk})\langle a|k\rangle \quad (\text{A1})$$

where $\langle a|k\rangle$ is the corresponding overlap integral. For a simple and approximate evaluation of this integral, the Slater-type adsorbate wavefunction $|a\rangle$ [24] with quantum number n_a and orbital exponents ξ_a is assumed to be distributed within a sphere of radius $2n_a/\xi_a$. The overlap integrals are determined by the product of the two wavefunctions at the centre of the overlap region (x_a, y_a, z'_a) multiplied by their overlap volume V_0 , i.e.

$$\begin{aligned} \langle a|k, 1\rangle &= (2V_0/\sqrt{V_a V}) \sin(k_3 z'_a) \cos(x_a k_1 + y_a k_2) \\ \langle a|k, 2\rangle &= (2V_0/\sqrt{V_a V}) \sin(k_3 z'_a) \sin(x_a k_1 + y_a k_2) \end{aligned} \quad (\text{A2})$$

where $V = L_1 L_2 L_3$, and

$$V_a = \frac{4\pi}{3} \left(\frac{2n_a}{\xi_a} \right)^3$$

is the volume of the sphere within which the atomic wavefunction of the adsorbate is assumed to be distributed. In this expression, the adsorbate is located at (x_a, y_a, z_a) implicitly, and $z'_a = \frac{1}{2}(z_a - 2n_a/\xi_a)$.

The diagonal elements of the Hamiltonian matrix are selected by the following forms:

$$H_{ii} = \begin{cases} -I_i & i \in \text{adsorbate} \\ -E_d & i \in \text{d state} \\ -E_\Gamma + h^2 k^2 / 2m & i \in \text{plane wave} \end{cases} \quad (\text{A3})$$

with I_i the ionisation potential for atomic orbital i [25] and E_d the centre of the d band relative to the vacuum level for transition-metal surface, which is evaluated from the sum of electron work function and energy difference from d band centre to Fermi level estimated from the known bulk band structure. Work functions for most transition-metal surfaces are already known from experimental measurements [22]. For Cu(100) and W(100), for example, E_d are chosen to be 7.9 (4.6 + 3.3) and 6.1 (4.6 + 1.5) eV, respectively. E_Γ represents the energy value at the Γ point for the free-electron band and its position relative to the d band centre is also given by Harrison [11, 12].

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