

The Electronic Configuration of Platinum (110) Surface Atoms with the Least Coordination Number

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A model calculation using the Hubbard model in conjunction with the chemisorption theory based on the Hartree-Fock approximation has been carried out to study the ground-state configuration of Pt (110) surface atoms with the least coordination number. It is found that for these atoms the number of 5d holes is larger than 2 and the 6s orbital is almost filled in contrast to the common belief that their configurations lie between that of a free atom and the bulk of crystal. The results also suggest a trend that the d electron transfer from the corresponding surface atom to the bulk is maximum in group VIII metals for a given transition series.

I. INTRODUCTION

ONE commonly considered that the ground-state configuration of the surface atom lies between that of a free atom and the bulk of crystal. The ground state of a free Pt atom has $5d^96s$ configuration and the number of s electrons per atom in the metallic platinum is 0.4^(1,2). Thus one expects that the number of 5d electrons of Pt surface atoms will lie between 9 and 9.6.

Tsang and Falicov⁽³⁾ showed that for the edge atoms at a stepped metallic-platinum surface there is 0.8e of 5d electron transferred from the edge atom to the bulk. The d electron transfer was viewed as caused by and proportional to a difference of electronic potential between the edge atom and the bulk, which arises from sp conduction electrons. It was derived from dipole-moment measurements, however, that the net charge on the edge atom of a stepped metallic-platinum surface is only 0.16e and the net charge on a Pt adatom on Pt(111) surface is only 0.48e⁽⁴⁾.

The charge state of 5d transition metal adatoms on tungsten has been studied by Muscat⁽⁵⁾ using the Hubbard model. It was shown that the charge transfer is very small for large values of intra-atomic Coulomb repulsion. The measurements of Auger spectra, however, indicated that the intra-atomic Coulomb repulsion of 3d transition metals is strongly reduced by the relaxation energy⁽⁶⁾. The dominant part of the relaxation energy arises from the electronic and lattice polarization effects⁽⁶⁾. Since the 5d transition metals have a broader valence band, a strong reduction of the intra-atomic Coulomb repulsion may be expected for these metals.

In this study a model calculation is carried out to show that the d electron transfer of certain Pt surface atoms with the least coordination number is large, more than 1, and the 6s orbital is almost filled. The existence of more than two unpaired 5d electrons extends the usefulness of a previous work⁽⁷⁾, which concerned the dissociative chemisorption of the hydrogen molecule by a

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single *Pt* surface atom, to low temperatures.

The results also roughly imply a trend that the *d* electron transfer from the particular surface atom to the bulk is maximum in group VIII metals for a given transition series. A more precise description of the charge state of these surface atoms is possible if the effective intra-atomic Coulomb repulsion is known for these transition metals.

II. THE MODEL CALCULATION AND RESULTS

A *Pt* (110) surface atom with the least coordination number is regarded as an **adatom** which lies on top of an atom of the surface layer as shown in the figure; this geometry may be physically realized as a surface defect or regarded as a limiting case.

The valence-electron system is divided into localized *W*-electron and itinerant *sp*-electron parts. The *5d* electrons are considered to move in a self-consistent field arising from screening *sp* electrons, meanwhile the self-consistent field is determined by the response of *sp* electrons to the distribution of *5d* electrons through the use of an effective charge, Z_{eff} , on the adatom. $Z_{eff} = 11 - n_s - n_d$, where n_s and n_d are the mean number of *6s* and *5d* electrons respectively at the adatom defined by the components of the *6s* and the *5d* atomic orbitals.

Firstly, we describe the self-consistent field. The surface boundary can be determined by the scheme of the jellium model⁽⁸⁾. In our case the distance, z_0 , of the adatom from the surface boundary is $3.93a_0$ (a_0 is the Bohr radius); this distance enables us to describe the electronic potential seen by an electron at the adatom by image potentials derived from density-functional formalism with the jellium model⁽⁸⁻¹⁰⁾. The small relaxation of the surface layer has been ignored⁽¹¹⁾. The total image potential in cylindrical coordinates takes the form

$$V_{im} = -\frac{2Z_{eff}}{\sqrt{(z_0 - 2\delta_1 + z)^2 + \rho^2}} \frac{1}{2(z - \delta_2)} \quad \text{ryd } z \geq 0 \quad (1)$$

where z is in normal direction and $z=0$ is the surface boundary. $\delta_1 = 0.82a_0$, which is employed from the results of density-functional calculation by Appelbaum and Hamann⁽⁹⁾ with r_s (the Wigner-Seitz radius) $= 2.89a_0$, which corresponds to 1.0 *sp* conduction electrons per atom (by analogy with

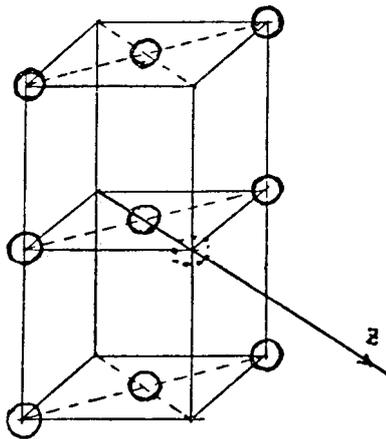


Fig. I. The surface geometry. The surface atoms on the outermost (110) plane and the particular atom (the adatom) are illustrated by circles and the dotted circle respectively. (Pt has an fcc structure)

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Ni) instead of 0.4 based on an allowance for $sp-d$ hybridization^(1,12). As given by Appelbaum and Hamann, the effective position of the image plane, δ_2 , remains constant when $z \geq 3a_0$ and decreases almost straightly down to a negative value when $z \leq 3a_0$. Here we approximate that $\delta_2 = \delta_1$ when $z \geq 3a_0$ and for smaller z , δ_2 decreases straightly down to $-1/2W$. Where W is the depth of the potential well, with this approximation the electronic potential is continuously connected at $z=0$. W is evaluated as the sum of the work function, ϕ , and the Fermi energy of sp electrons, i.e. about 0.44 ryd for $r_s = 2.89a_0$ if the free electron model is assumed⁽⁹⁾. $\phi = 5.7\text{eV}$ for the (111) surface⁽¹³⁾, here it is assumed to be smaller by 0.08eV for the (110) surface; this value is obtained by analogy with the tungsten metal^(*).

The $5d$ electrons of the adatom and d -band electrons of the substrate are described by an extension of the multiband Hubbard model⁽¹⁴⁾ as

$$\hat{H}_d = \hat{T} + \hat{V}_c$$

with

$$\begin{aligned} \hat{T} &= \sum_{i,j,\nu} t_{ij\nu} a_{i\nu}^+ a_{j\nu} \\ \hat{V}_c &= \frac{1}{2} \sum_{i,\nu,\nu'} a_{i\nu}^+ a_{i\nu}^+ a_{i\nu'} a_{i\nu'} + \frac{1}{2} U_d \sum_{\nu,\nu'} a_{d\nu}^+ a_{d\nu}^+ a_{d\nu'} a_{d\nu'} \end{aligned} \quad (2)$$

where ν and ν' denote the ten $5d$ spin-orbitals, the summation in \hat{T} is over all atoms, the first summation in \hat{V}_c does not include the adatom, and the last term accounts for the effective intra-atomic Coulomb interactions at the adatom. Strictly speaking, U of the atoms in the surface layer is different from bulk U owing to a different relaxation energy, here it is approximated as the same; this may be appropriate for low index surfaces. U_d is the effective intra-atomic Coulomb repulsion of $5d$ electrons at the adatom. The interactions between $6s$ electrons of the adatom and d -band electrons of the substrate can be incorporated into finding the resonance level and the half-width of the $6s$ electrons of the adatom.

Following Thalmeier and Falicov⁽¹⁴⁾, the ground state S -electron energy, E_d , is given by $E_d = T_o + V_{co} + E_B + E_c$. Written explicitly

$$T_o = N_m C_o n_m + C_o n_d \quad (3)$$

$$V_{co} = \frac{1}{2} U N_m n_m (n_m - 1) + \frac{1}{2} U_d n_d (n_d - 1) \quad (4)$$

$$E_B = \langle \hat{T} \rangle - T_o \quad (5)$$

$$E_c = \langle \hat{V}_c \rangle - V_{co} \quad (6)$$

Where $\langle \rangle$ denotes the expectation value, n_m is the mean number of $5d$ electrons in each substrate atom, and N_m is the total number of substrate atoms. The difference in n_m of the surface layer from the bulk is ignored. T_o and V_{co} account for the total S -electron energy when hopping integrals, $t_{ij\nu}$, are absent. E_B arises from the the hopping integrals and it is identified as the d -band energy. E_c is the correlation energy, which arises from the fluctuation of d spin-orbital occupation number.

It is known that the binding energy of the transition metal adatoms adsorbed on a transition metal surface is largely due to d electrons⁽¹⁵⁾; $d-sp$ hopping is of secondary importance. The ground-state n_d can be approximately obtained by minimizing E_d with respect to the variation of n_d , and we find

$$n_d = \frac{1}{2} + \frac{1}{U_d} \left[U \left(n_m - \frac{1}{2} \right) - \partial E_B / \partial n_d - \partial E_c / \partial n_d \right] \quad (7)$$

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The effective intra-atomic Coulomb repulsion of an adatom has been shown to be reduced by twice the total image potential from its atomic value, $U_d^{(16,17)}$. U_d is estimated to be 1.06 ryd using Herman-Skillman 5d orbitals⁽¹⁸⁾ (which is obtained by equating the total Coulomb energy⁽¹⁹⁾ of the 5d shell to $\frac{1}{2}U_d n(n-1)$ with $n=9$). It has been determined from Auger spectra that the effective intra-atomic Coulomb repulsion of 3d electrons in metallic nickel is about 0.3 ryd⁽⁶⁾. The same experimental method can be used to find U in metallic platinum. The radius of 5d orbitals of the platinum atom is larger than that of 3d orbitals of the nickel atom; one expects a smaller U for the platinum metal. On the other hand, the binding energy calculations of 5d transition metal adatoms on tungsten by Muscat⁽⁵⁾ and Newns⁽²⁰⁾ suggested $U \geq 0.4$ ryd. Here a range of U values from 0.2 ryd to 0.4 ryd has been considered.

Since E_B is derived from coupling potentials, one can approximate $\partial E_B / \partial n_d$ by $C_o + t - E_F$, where t is the sum of the total image potential and the atomic potential of the nearest neighbor atom seen by a 5d electron at the adatom. The physical meaning is that an extra 5d electron appears at the adatom is statistically coming from a substrate d electron on the Fermi surface, while at the adatom it has an energy C_o and feels an effective potential t . C_o is the center of the d-band and we find $C_o - E_F \cong -0.23$ ryd⁽²¹⁾. Using Herman-Skillman 5d orbitals and atomic potential⁽¹⁸⁾, whose tail has been modified by a factor of 0.4 to account for the loss of delocalized s electrons, t is estimated to be about 0.17 ryd (for $Z_{eff} = 1.5$). Although this approximation may be rough, it can be seen from equation (7) that $\partial E_B / \partial n_d$ term is not a dominant term unless n_m is small.

The last term $\partial E_c / \partial n_d$ can be divided into two parts, $\partial E_{cm} / \partial n_d$ and $\partial E_{cd} / \partial n_d$, which are contributed from the substrate and the adatom respectively. In platinum metal there are only two unfilled d bands; one of them is almost filled^(12,14). Using Thalmair and Falicov's results⁽¹⁴⁾ and $n_m = 9.6$, one obtains $\partial E_{cm} / \partial n_d \cong 0.16U$. Since the adatom has a much lower coordination number, the fluctuation of 5d orbital occupation number is smaller than that of bulk atoms⁽¹²⁾ (in the atomic limit E_c vanishes), and then $\partial E_{cd} / \partial n_d$ is negligible in comparison with other terms in equation (7).

Using the above data, equation (7), and the equation for Z_{eff} , one finds $Z_{eff} = 1.73, 1.53,$ and 1.34 respectively for $U=0.2$ ryd, 0.3 ryd, and 0.4 ryd; these values correspond to $n_d = 7.27, 1.47,$ and 7.66 respectively.

The chemisorption theory based on the Hartree-Fock approximation⁽¹⁾ is employed to treat the interaction of 6s electrons of the adatom with the substrate. For nonmagnetic case, the resonance level, ϵ_r , is given by

$$\epsilon_r = \epsilon_a + \langle V_{im} \rangle + \frac{1}{2} n_s U_s + A(\epsilon_r) \quad (8)$$

where U_s is the effective intra-atomic Coulomb repulsion of 6s electrons at the adatom and ϵ_a is the effective atomic level when the coupling with substrate electrons is absent. $A(\epsilon_r)$ and the half-width, $\Delta(\epsilon_r)$, are the real part and the imaginary part respectively of $\sum_k |V_{ak}|^2 / (\epsilon_r - \epsilon_k - i\delta)$, where ϵ_k is the energy level of the substrate state $|k\rangle$ and V_{ak} is the matrix element of the atomic potential of the adatom between the 6s orbital and the substrate state.

The effective atomic level, ϵ_a , equals the ground state level of a free Pt atom, i.e. -0.647 ryd with respect to the vacuum level⁽¹⁹⁾, plus $\Delta\epsilon_a$. $\Delta\epsilon_a$ is the shift of the atomic level due to the increase of the effective atomic charge Z_{eff} from 1. Using Herman-Skillman 6s orbital, one finds that the intra-atomic Coulomb repulsion between 6s electrons, U_s , is 0.53 ryd. As stated previously $U_s = U_d - 2V_{im}$ ^(16,17). The substrate states can be divided into sp like states and d like states; the latter

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can be transformed into an atomic orbital representation") and it is a reasonable approximation to consider only the $5dz_2$ orbital of the nearest neighbor surface atom.

Employing the eigenfunctions and eigenvalues of a potential well with well depth W for sp like states and Herman-Skillman orbitals and atomic potential (whose tail is modified by a factor of Z_{eff} and cutoff inside the substrate), it can be shown that $\Delta(\epsilon_r) \ll E_F - \epsilon_r$ for $1.34 \leq Z_{eff} \leq 1.73$. These show that the resonance level is almost filled, i.e. $n_s \approx 2$; this result is consistent with the assumption given in the calculation of Z_{eff} and n_d .

III. DISCUSSION

The results show that the d electron transfer from the adatom to the substrate is large, i.e. between 1.34 and 1.73, and almost a $6s$ electron is gained by the adatom in contrast to the common belief that n_d and n_s lie between that of a free atom and the bulk of crystal. The net charge of a Pt adatom on the Pt (111) most closely packed surface is $0.48e$ as stated previously. For the present geometry the net charge will be larger"); with our results this argument suggests that $U \leq 0.3$ ryd.

In a previous work⁽⁷⁾, it has been shown qualitatively the existence of two channels of a pair of hydrogen atoms around a platinum surface atom which protrudes from an otherwise smooth surface, one corresponds to a hydrogen molecule and another a pair of dissociated atoms, provided the particular surface atom has two unpaired $5d$ electrons. Our results show that this may be physically realized even at low temperatures.

Equation (7) is based on the neglect of the direct contribution of sp electrons to the binding energy. It is well known that the cohesive energy of the transition metals is largely due to d electrons; the same appears to be true for the binding energy of transition metal adatoms adsorbed on a transition metal surface⁽¹³⁾. Within the validity of this argument, equation (7) is not only approximately applicable for platinum but also for other transition metals, especially those on the right hand side of a transition row due to a larger number of d electrons.

It can be seen from equation (7) that for larger n_m the difference, $n_m - n_d$, is roughly proportional to n_m and $(1 - U/U_d)$. $n_m - n_d$ can be used to characterize the d electron transfer. Due to the similarity in the trend of electronic structures^(22,23), it is sensible to assume that the trend of the effective intra-atomic Coulomb repulsion, U , of the $3d$ transition series is adoptable for $4d$ and $5d$ series; i.e. U increases as one approaches the right end of a given series⁽⁶⁾. Owing to similar d orbitals and atomic radii, U_d^* as well as U_d is roughly a constant for a given transition series. Then equation (7) implies a maximum $n_m - n_d$, roughly the d electron transfer, in group VIII elements. This implication qualitatively explains the experimental results of Besocke *et al.*⁽⁴⁾, in which the net charge of the gold and the tungsten adatoms on gold and tungsten surfaces respectively are both about one half smaller than that of platinum. More precise comparison using the extension of the present model calculation is possible if U as well as U_d is known for these metals.

IV. CONCLUSION

Our results reveal that in the ground state the particular surface atom considered has more than two $5d$ holes and an almost filled $6s$ orbital. The net charge on this atom calculated is compatible with the experimental result.

The existence of two unpaired $5d$ electrons suggests that the dissociative chemisorption of the hydrogen molecule by a single Pt surface atom is probable even at low temperatures.

Our results also suggest a maximum d electron transfer from the surface atom to the bulk in group VIII metals for a given transition series.

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