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A simple model for the adsorption of a monovalent atom on a metal surface and the field desorption

I V Abarenkov† and L E Bar'yudin‡

Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK

Abstract. The adsorption of an atom with one valence electron on a metal surface and the field desorption of this atom are considered in this paper. A very simple one-electron model is shown to describe properly the general features of the processes considered.

1. Introduction

The problem of the adatom–metal surface electronic structure and their interaction has a long history. There have been various calculations of different complexity and precision (see, for example, [1–6]). The *ab initio* quantum mechanical calculations of the adatom–metal surface, especially in the case of an applied external electric field, are very complicated due to the complexity of the system, its low symmetry, the large number of competing interactions, and the non-linearity of the corresponding mathematical problem. High-precision calculations are very time-consuming and therefore are rare for the system considered. For simpler calculations, it seems expedient to make, if possible, all the necessary approximations from the very beginning, when they are not obscured by complicated mathematical expressions, and to consider the result as a physical model. Not claiming high precision, such models may nevertheless provide a reasonably good description of the system and can qualitatively explain various trends. In the present paper, we will consider a very simple model and will show that it enables us to describe the adsorption of a monovalent atom on a metal surface and the field desorption of it.

2. The one-electron problem

For the sake of simplicity we assume that the metal surface is the structureless x, y plane, the z axis being directed into the vacuum. We will employ the adiabatic approximation, and will consider only the motion of the adatom perpendicular to the surface. So the X, Y coordinates of the adatom are equal to zero, the adatom–surface distance Z being the only adiabatic variable. Next, we will replace the many-electron metal–adatom problem by the problem for a single-valence electron moving in the given

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† On leave from Physics Department, Leningrad University, Leningrad, USSR.
‡ Permanent address: Physics Department, Leningrad University, Leningrad, USSR.

effective field. We will consider all core electrons of the atom and all the electrons of the metal as the source of the field for the valence electron. So the electronic equation in the adiabatic approximation is

$$\hat{H}(r, Z)\psi(r|Z) = E(Z)\psi(r|Z) \tag{1}$$

where

$$\hat{H}(r, Z) = -\tfrac{1}{2}\Delta + V_{at}(r - Ze_z) + V_{met}(r). \tag{2}$$

(Atomic units will be used throughout the paper.) In (2) V_{at} is the effective field potential of the atomic core and V_{met} is the effective field potential of the metal and its surface. The adiabatic potential in this case is

$$W(Z) = E(Z) + U(Z) \tag{3}$$

where $U(Z)$ is the interaction energy between the atomic core and the metal.

3. The potential

The effective field potential of the atomic core is evident. Assuming the core to be rigid, it is convenient to employ the semi-empirical model pseudopotential

$$V_{at}(r) = \begin{cases} -A_2 - (A_0 - A_2)\hat{P}_0 - \gamma r^2 \hat{P}_1 & \text{if } r < R_M \\ -1/r & \text{if } r > R_M \end{cases} \tag{4}$$

which is non-linear in the angular quantum number l. In (4), R_M is the atomic core radius, P_l is the projection operator onto the subspace of spherical harmonics with given l, and A_0, A_2, and γ are adjustable parameters. The functional dependence on r in the $l = 1$ component was chosen to make the evaluation of matrix elements simple. The parameters are adjusted such that the energy of the electron in the potential $V_{at}(r)$ coincides with the negative of the experimental values of the energy necessary to remove a valence electron from the corresponding state in the atom to infinity.

The effective field potential of the metal is less evident. Because we reduce the total problem to the one-electron one, the potential $V_{met}(r)$ cannot simply be the pseudopotential of atomic cores of the metal. It should also describe the influence (screening) of conduction electrons of the metal on one particular electron, which we consider to be the valence electron originally belonging to the atom. The following considerations help us to construct this potential. For the metal with surface we will use the jellium model with an appropriate value of the parameter r_s, assuming the positive background to be uniform in the half-space with $z < 0$ and to be abruptly terminated at $z = 0$. When the valence electron is in the atomic region the disturbance of the metal by the neutral atom is small and we can neglect it. In this case, the potential of the metal seen by the valence electron is zero. If the valence electron is inside the metal, it should be at the Fermi level. Therefore the potential for the valence electron in the metal is a potential well with constant depth equal to the negative of the work function. Next, if the valence electron is in the metal the atom becomes an ion and it induces charge in the metal. Because in the case considered

the induced charge in the semi-infinite metal is equal to 1, we will simply simulate the induced charge by the charge distribution of the valence electron. It is known [1] that the centre of mass of the induced charge is localized some distance z_0 away from the positive background. Therefore we will take the following simple expression for the pseudopotential of the metal with surface

$$V_{\text{met}}(r) = E_{\text{F}}\theta(z_0 - z) \qquad (5)$$

where

$$\theta(x) = \begin{cases} 1 & \text{if } x > 0 \\ 0 & \text{if } x < 0 \end{cases} \qquad (6)$$

and E_{F} is the Fermi energy with respect to the vacuum level. The values of z_0 for different r_s can be found in [1]. The stepped form of this potential is a rather crude model approximation but it makes the model easy and still results in reasonable accuracy.

4. The basis functions

Though (1) is the equation for one electron, it is three-dimensional and we will solve it with the help of an expansion of the wavefunction into the Gaussian orbitals basis set

$$\psi(r, Z) = \sum_k C_k g_{l_k m_k}(\zeta_k, \mathbf{R}_k; r). \qquad (7)$$

Here

$$g_{lm}(\zeta, \mathbf{R}; r) = N_l(\zeta)\rho^l \exp(-\zeta\rho^2)Y_{lm}(\nu, \varphi) \qquad (8)$$
$$r - \mathbf{R} = (\rho, \nu, \varphi)$$

is the Gaussian orbital (GO), $N_l(\zeta)$ is the normalization factor, Y_{lm} is the spherical function and $\mathbf{R}$ is the point of the orbital's localization.

Several different groups of GO were used in the present paper.

(i) Group of 1s GO localized on the adatom. The number of orbitals and parameters ζ_k were chosen to make this group a representative basis for the valence electron wavefunction of the ground state of the isolated atom.

(ii) Group of 2p GO localized on the adatom. These orbitals are to account for the deformation of the atomic orbital due to the surface and the external field. These GO were found by considering a single atom. When a homogeneous electric field F is applied to the atom, the valence electron wavefunction in the first-order perturbation theory becomes a linear combination

$$\psi(r) = \psi_0(r) + F\chi(r) \qquad (9)$$

of the s-function of the ground state $\psi_0(r)$ and the correction function $\chi(r)$ which has p-symmetry. The correction function was calculated in first-order perturbation theory, the model pseudopotential (4) being considered as the unperturbed one. The

2p GO basis was constructed to be representative for the correction function. The calculated dipole polarizabilities of the atoms coincide to within a few percent with their experimental values.

(iii) Group of 1s GO localized at different points on the z axis between the adatom and the metal and in the subsurface region of the metal. The parameters ζ of these orbitals and the distances between localization points were chosen to provide a sufficient coverage of the region between the adatom and the metal. Usually ζ was in the range 0.07–0.10 and the distance was 2.0–2.5 au.

(iv) A single diffuse 1s GO deep in the metal.

The total number of GO was typically about 15. A further increase of the number of basis orbitals changes the results only insignificantly, so the basis used can be considered as a representative one.

5. The adatom core–metal interaction energy

The interaction energy $U(Z)$ between the metal and the core of the adatom consists of two parts. The first is the interaction between the atomic cores of the metal and that of the adatom and the second is the interaction between the conduction electrons and the adatom core. The first is purely a Coulomb repulsion, and if the adatom core is outside the positive background, the electrostatic interaction energy between the point charge and the positive background could be taken instead of this Coulomb repulsion. The second can be calculated with the help of the model pseudopotential (4) and the one-electron wavefunctions of the conduction electrons. To calculate it, it is necessary to know the wavefunctions of all conduction electrons. But if we approximately replace the nonlocal model pseudopotential (4) by the local one

$$V_{\mathrm{at}}(\boldsymbol{r}) = \begin{cases} -A & r < R_{\mathrm{M}} \\ -1/r & r > R_{\mathrm{M}} \end{cases} \tag{10}$$

then not the individual wavefunctions, but only the total electronic density of conduction electrons will be required [2]. For that we can take the well known expression [7]

$$\rho(z) = \rho_0 \times \begin{cases} \exp(-\beta z)/2 & z > 0 \\ 1 - \exp(\beta z)/2 & z < 0 \end{cases} \tag{11}$$

where ρ_0 is the electron density in the bulk. Then for $U(Z)$ in the region $Z > R_{\mathrm{M}}$, we obtain

$$U(Z) = U_0\, e^{-\beta Z} \tag{12}$$

where

$$U_0 = -\frac{\pi \rho_0}{\beta^2} \left\{ e^{\beta R_{\mathrm{M}}} \left[1 + \frac{A}{\beta}(1 - \beta R_{\mathrm{M}}) \right] + e^{-\beta R_{\mathrm{M}}} \left[1 - \frac{A}{\beta}(1 + \beta R_{\mathrm{M}}) \right] - 2 \right\}.$$

6. Homogeneous electric field

In the case where the homogeneous electric field is applied to a metal with adatom, it is necessary to make several changes to the model. First, the potential energy $V_F(Z)$ of the electron in the applied field should be added to the operator $H(r, Z)$ in equation (2). This potential energy is equal to Fz for large positive z (vacuum) and it is equal to zero for negative z (metal), because the conduction electrons screen it. In our simple model, we will neglect the region where the actual screening takes place and will assume that

$$V_F(z) = Fz\,\Theta(z). \tag{13}$$

Second, the energy of the adatom core in the external field

$$V_i(Z) = -FZ \qquad Z > 0 \tag{14}$$

should be added to the adiabatic potential $W(Z)$. Third, in the calculation of $U(Z)$ it is necessary to employ $\rho(z + \delta z)$, the shifted density (11) of the conduction electrons, the shift δz being adjusted to reproduce the screening of the external electric field in the metal region.

7. Results and discussion

Calculations were performed for all the alkali adatoms and for hydrogen on jellium with r_s chosen to correspond to tungsten. The adiabatic potential $W(Z)$ was first calculated for the case with no external field present. As an example the adiabatic potential for lithium on tungsten is shown in figure 1. From this adiabatic potential, the equilibrium distance of the adatom from the surface, Z_0, the adsorption energy, E_a and the frequency ω of the adatom vibration perpendicular to the surface were calculated. The results are given in table 1, where they are compared with other theoretical and experimental data. The calculated values of Z_0 and E_a are in good agreement with other data. The values of ω show the correct trend, but for H, Rb and Cs are too large by a factor of 2.

Another characteristic of the metal–adatom system is the dipole moment, μ. To calculate μ it is necessary to know the electron density distribution of the system. The model under consideration employs the pseudo-potential method. This method produces correct energy and the pseudo-one-electron function ψ. To obtain the one-electron function one should orthogonalize ψ to the adatom core one-electron functions and, most essentially, to all metal one-electron functions. The latter were purposely excluded from the model to make it simple. Hence we are left with the pseudo-density $|\psi|^2$ only. As an example, the 'pseudo-density' for lithium on tungsten at the equilibrium position of the adatom is shown in figure 1. The 'pseudo-density' shows some general features of the valence electron density distribution, as can be seen from figure 1. Sometimes, depending on the physical system, orthogonalization results in only minor changes in the pseudo-one-electron function. In these cases the 'pseudo-density' can reproduce the valence electron density with reasonable accuracy, so one can simply use the 'pseudo-density' instead of the real density. But for the systems considered in the present paper, the values of μ calculated directly with the

Table 1. Adsorption parameters and the value of the desorption for alkali atoms and hydrogen on tungsten.

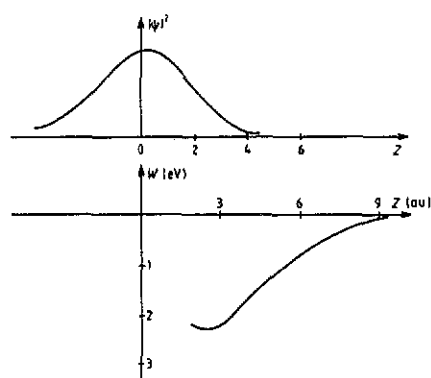| Adatom	Li	Na	K	Rb	Cs	H
E_λ (eV)						
Present work	2.35	2.4	2.9	3.4	3.8	2.6
Other data	2.75[a] [8]	2.9[a] [9]	2.9[a] [10]	2.83[b] [3]	2.7[b] [3]	3.16[b] [11]
	2.8[a] [12]	2.01[a] [10]			3.3[a] [13]	2.27[b] [14]
	2.5–2.8[a] [15]					2.5[b] [16]
						3.10[a] [17]
Z_0 (au)						
Present work	2.5	3.5	4.1	4.4	4.7	0.9
Other data	2.65[b] [3]	3.7[b] [3]	4.5[b] [3]	5.5[b] [3]	6.25[b] [3]	1.08[b] [18]
w (meV)						
Present work	40	25	18	12	10	230
Other data	56[b] [3]	24.7[b] [3]	13.7[b] [3]	6[b] [3]	4[b] [3]	136[b] [11]
						148[b] [14]
						130[a] [19]
μ (D)						
Present work	8.0	10.0	10.0	9.4	8.6	0.63
Other data	0.9[b] [3]	2.4[b] [3]	3.9[b] [3]	8[b] [3]	7–11[b] [3]	0.17[b] [11]
		3.5[a] [10]	5–6[a] [10]		6–8[a] [10]	0.14[b] [14]
F_d (V Å^{-1})						
Present work	0.9	0.8	1	1	1	7
Other data	0.8–1.0[a] [15]	0.7[b] [3]	0.4[b] [3]		0.3[b] [3]	5.6[a] [22]
		0.6[a] [10]	0.4[a] [10]		0.3[a] [10]	3.85[a] [8]
			0.5[a] [20]			3.78[b] [23]

[a] Experiment.
[b] Theory.

Figure 1. Li on tungsten at zero applied field. The adiabatic potential $W(Z)$ (in eV) and the pseudo-density along the Z axis in the equilibrium position of the adatom.
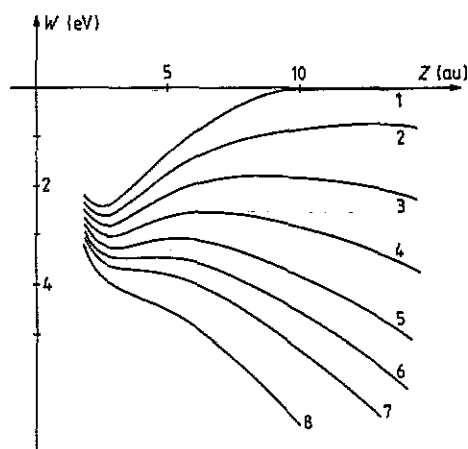

Figure 2. Li on tungsten; the adiabatic potential $W(Z)$ for different value of applied field F (in V Å^{-1}). 1: $F = 0$, 2: $F = 0.2$, 3: $F = 0.4$, 4: $F = 0.6$, 5: $F = 0.8$, 6: $F = 0.95$, 7: $F = 1.1$, 8: $F = 1.4$.

use of 'pseudo-density' are correct only within the order of magnitude (see table 1). They are too large, indicating that the orthogonalization to the metal one-electron functions essentially reduces the valence electron density in the metal region, and as a result pushes its centre of gravity much closer to the adatom. Therefore in the model considered the pseudo-one-electron function ψ is good for calculation of the energy values and not for other physical quantities, and the simple direct use of the 'pseudo-density' is justified for qualitative arguments only. To calculate the dipole moment μ with the help of the obtained pseudo-one-electron function ψ one should employ the full orthogonalization procedure first. This is a possible but tedious task which requires all the metal one-electron functions and goes against to the simplicity of the model.

After the zero-applied-field case was examined, the adiabatic potential was calculated for several values of the applied electric field strength, F. This adiabatic potential shows a Shottky barrier if the field is not too strong. It can be seen, for example in figure 2, where the adiabatic potentials for the lithium on tungsten system are shown. The value of the field for which this barrier vanishes was taken to be the desorption field. Its calculated values are given in table 1. They are in reasonable agreement with other data.

The calculated pseudo-one-electron function ψ has a consistent behaviour when the metal–adatom distance increases. It shows that for small metal–adatom distances there is a charge partition between adatom and metal. For large metal–adatom distances the charge resides fully in the adatom if there is no external electric field and fully in the metal if the external field is applied. The example is shown in figure 3 for the lithium-on-tungsten system.
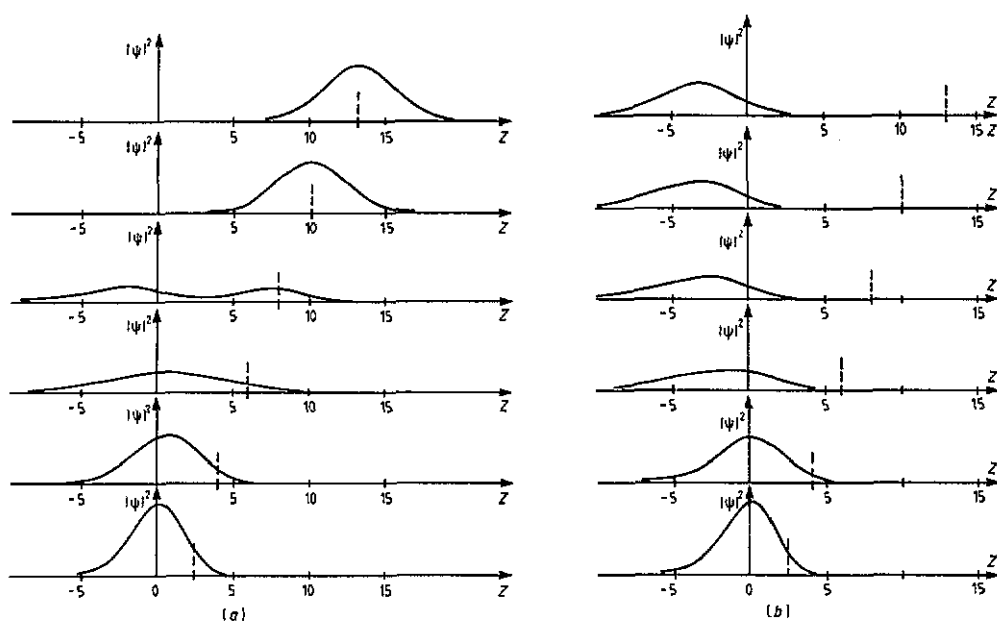

Figure 3. Li on tungsten. The pseudo-density along Z axis for different positions of adatom shown by a broken line; (a) zero applied field, (b) applied field 0.8 V Å^{-1}.

All the data presented here confirm that the very simple model introduced can

describe the general features of adsorption and field desorption of an adatom on a metal surface.

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