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Self-Consistent Calculation of Atomic Adsorption
on Metals in High Electric Fields

by

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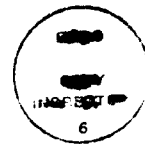
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1. Introduction

Imaging of single atoms in the field ion microscope is believed to occur as a result of local field enhancement around kink sites and around single metal atoms on flat crystal planes. These local electric fields of the order of $V/\text{\AA}$ arise, via Poisson's equation, from local enhancements of the surface electron density. To understand this phenomenon from a microscopic point of view, it is mandatory to calculate the electronic charge distribution and the resulting electrostatic field self-consistently.

Classical electrostatic theory predicts that the electrostatic potential around a hemispherical protrusion of radius R on an otherwise flat and structureless metal surface is given by⁽¹⁾

$$\phi = -4\pi\sigma_0 z(1 - R^3/r^3) \quad (1)$$

where σ_0 is the excess charge far from the protrusion and r is measured from the center of the protrusion. Locally the excess charge redistributes itself into

$$\sigma = \sigma_0(1 - R^3/r^3) \quad (2)$$

on the plane, and

$$\sigma = 3\sigma_0 z/R \quad (3)$$

on the sphere. We note that, at the apex of the boss, the electric field is three times its value at infinity.

The first quantum mechanical calculation of the self-consistent charge density and electric field distribution at a metal surface was performed by Lang and Kohn⁽²⁾ for a structureless jellium surface using the local-density approximation to density functional theory. A systematic study of this problem was recently performed by Gies and Gerhardt⁽³⁾ and also by Schreier and Rebentrost⁽⁴⁾. Including the crystal structure, Inglesfield has performed self-consistent field calculations for Al and Ag surfaces^(5,6). (For a recent review of field adsorption, field desorption and field evaporation, see ref.7.)

To understand field effects in the field ion microscope, one would like to calculate the local field at kink sites or around single atoms on densely packed planes of transition metals. As a model of the latter, we will report, in this paper, self-consistent calculations of the electric field around a metal atom adsorbed on a structureless jellium surface using the local density functional theory. As examples, we consider a light and a medium heavy metal atom, Ti and Nb, respectively, on a jellium metal with a Wigner-Seitz radius $r_s=3.0$ bohr. We will restrict ourselves to the polarity where the field points away from the surface, appropriate for the field ion microscope. Although our model describes the chemisorption of metal atoms on a free electron metal in the presence of a field, we will see below that the results have quite general features that allow a discussion of field effects in chemisorption on transition metals.

In the next section we collect the relevant equations and specify the boundary conditions. In the following sections we discuss numerical examples, i.e. the adsorption of Nb and Ti atoms on jellium in the presence of an external field. We will recover the field enhancement, described classically by (1-3), albeit of smaller magnitude. We will also produce the

adsorption potential well for these atoms and calculate the evaporation field strength above which surface atoms are no longer bound to the surface. Despite the simplicity of the jellium model we find very good agreement with experimental values, and also with earlier semi-empirical calculations based on the ASED-MO method^(7,8). We will also discuss the dipole moment and the polarizability of the adsorbed atom to make a connection with some experimental results.

2. The Model

In the introduction we have described electric fields by using classical electromagnetic theory, which assumes that the surface of a metal is a mathematical plane with excess charges and a dipole layer at which the normal component of the electric field drops discontinuously to zero, at least for a perfect conductor. On real surfaces, however, the electron distribution and electric fields vary smoothly over distances of a few angstroms. A simple model^(2,9) that exhibits these features is the jellium model of a metal, in which it is assumed that the ionic lattice can be smoothed into a uniform positive charge density n_+ that drops to zero abruptly half a lattice constant above the topmost layer of ion cores. In front of this jellium metal we add a metal atom⁽¹⁰⁾ around which we will study the local electron and field distribution within the framework of density functional theory. The latter determines the exact ground-state electron (number) density as the self-consistent solution of the equations

$$n(\mathbf{r}) = \frac{m}{\pi \hbar^2} \sum_{\nu} \Theta(\epsilon_F - \epsilon_{\nu}) |\psi_{\nu}(\mathbf{r})|^2 \quad (4)$$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}[n; \mathbf{r}] - \epsilon_\nu \right) \psi_\nu(\mathbf{r}) = 0 \quad (5)$$

In the local-density approximation, the effective potential

$$v_{\text{eff}}[n; \mathbf{r}] = \phi(\mathbf{r}) + \mu_{\text{XC}}(n(\mathbf{r})) \quad (6)$$

is the sum of the electrostatic potential as seen by an electron, determined from Poisson's equation

$$\nabla^2 \phi(\mathbf{r}) = 4\pi e [n_+ - n(\mathbf{r})] \quad (7)$$

and the exchange and correlation contribution, μ_{XC} , as discussed in refs. 2 and 9. $e > 0$ is the elementary charge.

To study chemisorption of an atom on jellium, one rewrites (5) in terms of a Lippmann-Schwinger equation⁽¹⁰⁾

$$\psi^{\text{MA}}(\mathbf{r}) = \psi^{\text{M}}(\mathbf{r}) + \int d^3\mathbf{r}' G^{\text{M}}(\mathbf{r}, \mathbf{r}') \delta v_{\text{eff}}(\mathbf{r}') \psi^{\text{MA}}(\mathbf{r}') \quad (8)$$

where ψ^{M} is the solution of (5) in the absence of the adsorbed atom, G^{M} is the Green's function of the bare metal and δv_{eff} is the difference of the effective potential (6) with and without the adsorbed atom. Because $\delta v_{\text{eff}}(\mathbf{r})$ approaches zero rapidly outside the adatom, one can restrict the integral in (8) to a sphere centered at the adatom, bounded by a surface S outside of which δv_{eff} is negligible.

To include an external electric field, one must add an excess surface charge to the metal. This is done first in the bare-metal problem by impos-

ing the condition

$$\sigma_0 = e \int_{-\infty}^{\infty} (n_+ \theta(-z) - n^M(z, F_0)) dz = F_0/4\pi \quad (9)$$

on the charge density of the bare metal, leading to wavefunctions $\psi^M(\mathbf{r}, F_0)$ and electron densities $n^M(\mathbf{r}, F_0)$ that depend explicitly on the field strength, F_0 , far from the surface. In the presence of the adatom one then requires that outside the sphere S

$$n^{MA}(\mathbf{r}; F_0) \rightarrow n^M(\mathbf{r}; F_0) \quad \text{for } |\mathbf{r}| \rightarrow \infty \quad (10)$$

which acts as a boundary condition on the solution of (8). Thus, the effect of the external electric field is imposed in the metal surface-adatom system through the condition (9).

While the external electric field does not change the structure of the one-electron equations, it does affect the numerical procedure. In the absence of external electric fields, the effective potential of a bare metal, $v_{\text{eff}}[n^M; z]$, will approach a constant for $z \rightarrow \infty$, usually taken as the zero of energy. However, in the presence of an external electric field of asymptotic strength F_0 , $v_{\text{eff}}[n^M; z]$ will grow as $eF_0 z$ for large z . It is then advantageous to choose the Fermi energy as the energy reference, $\epsilon_F = 0$. With this choice the energies of all occupied levels are negative.

To solve (8), one represents the wavefunctions with indices E, m and l , ψ_{Eml} , as $\mathbf{r}$ -dependent linear combinations of free-particle solutions, following ref. 10,

$$\psi_{Em1}(r) = \sum_{l'=0}^{\infty} \left[C_{Em1l'}(r) j_{l'}(pr) + S_{Em1l'}(r) h_{l'}^+(pr) \right] Y_{l'm}(\Omega). \quad (11)$$

Here $p = \sqrt{E}$ and $j_{l'}$ and $h_{l'}^+$ are the spherical Bessel functions. A complication arising in the presence of an electric field is the fact that the potential-energy barrier of field adsorption varies from several eV, i.e. the cohesive energy in the absence of the field, down to zero at the evaporation field strength. Recalling that the theory calculates the energy difference ΔE_t between the bare metal surface and the metal surface-adatom system, i.e. the total energy of the adatom of the order of 10^5 eV for Ti and Nb, we need a relative precision for the total energy difference of the order of about 10^{-7} .

3. Binding Energies and Energy Barriers

We now present numerical results for two systems, titanium and niobium, respectively, on a jellium with $r_s=3.0$ bohr.

In Fig.1, we show the adiabatic energy curves for niobium on jellium for several field strengths. In zero field the depth of the surface potential is 5.2eV, which is, not surprisingly, somewhat less than the cohesive energy of Nb, 7.47eV, because the jellium lacks p- and d-orbitals. This deficiency is also the cause of the rather weak repulsion at short distances. As we apply a field, we note a shift of the potential minimum by about $0.2 \text{ \AA}$ away from the surface. We will trace this shift to a transfer of electronic charge from outside the adatom to the region between the adatom and the surface. With a field applied, the ground state energy curves must assume an asymptotic form $-eF_0 z$ for large z , appropriate for a singly charged positive ion. Ionization of the adatom can occur when its highest occupied

level is lifted by the field energy term, $eF_0 z$, above the Fermi level of the jellium. If the ionization level were not shifted and broadened by the interaction with the metal, the changeover to the asymptotic form would happen abruptly at the apex of the potential energy curve, i.e. at the point where the diabatic energy curves for the neutral and ionic species cross. For the fields chosen for Fig.1, the apex is so close to the metal surface that considerable interaction between the adatom and the metal is still in effect. This results in a considerable broadening of the ionization level of the adatom, so that only partial charge draining occurs in the apex region.

We will call the energy difference between the minimum of the surface potential and the local maximum at its apex, the activation energy, $Q(F_0)$, for ionization. In zero field, the activation energy is equal to the binding energy of the adatom. We note that the activation energy becomes zero for the evaporation field strength which we estimate for Nb on jellium to be $3.6\text{V}/\text{\AA}$, which compares very favorably with the experimental value for Nb, $F_{\text{ev}}=3.5\text{V}/\text{\AA}$. Similar results are obtained for Ti. Binding and activation energies are collected in Table 1.

It has been suggested⁽⁸⁾ that the field dependence of the activation energy for different metals obeys a universal scaling law if one plots $Q(F_0)/Q(F_0=0)$ as a function of $f=F_0/F_{\text{ev}}$. In a simple model, this scaling law is given by

$$Q(F_0)/Q(F_0=0) = \sqrt{1-f} + \frac{1}{2}f \ln[(1-\sqrt{1-f})/(1+\sqrt{1-f})] \quad (12)$$

Experimental data on tungsten⁽¹¹⁾ and theoretical results obtained by the

ASED-MO method⁽⁸⁾ have confirmed this conjecture, as do the present results for Ti and Nb.

4. Charge Density and External Electrostatic Field

In Fig.2 we show the electron density shift

$$\delta n(\mathbf{r}, F_0) = n(\mathbf{r}, F_0) - n(\mathbf{r}, F_0=0) \quad (13)$$

due to the applied field, demonstrating an overall charge transfer from the region outside the adsorbed atom into the region between the atom and the bulk and further into the bulk. From (13) we can calculate, via Poisson's equation (7), the external electrostatic potential as the difference of the total electrostatic potential in the presence of an excess charge of density $\sigma_0 = F_0/4\pi$, and in the absence of it,

$$V_{\text{ext}}(\mathbf{r}) = V_{\text{es}}(\mathbf{r}, F_0) - V_{\text{es}}(\mathbf{r}, F_0=0) \quad (14)$$

Equipotential contours are plotted in Fig.3 for Ti and Nb. The expulsion of the external field from the region of the metallic adatom is beautifully demonstrated, the effect being larger for the heavier Nb atom. To compare this quantum mechanical result with the classical theory contained in (1-3), we have approximated the adsorbed atom by a hemispherical boss with the radius chosen in such a way that the zero equipotential lines coincide at the apex. The result of this classical fit is also shown in Fig.3. Except on the sides of the adatoms, the agreement between the quantum mechanical and classical theories is quite good, at least at the semi-quantitative level. There are some differences, of course, if we look at deta-

ils, which we do in Fig.4, where we plot the external field along a line through the apex of the adatom. Compared with the field in the absence of the adatom, we again note the expulsion of the field from the adatom region which results in an enhancement of the field just outside the adatom. We note, however, that this field enhancement at the apex is not as much as classical theory predicts, i.e. a factor 3. Rather, the partial field penetration into the adatom results in a smearing out of the field as a reflection of the adjustability of the electronic distribution at the surface, reducing the enhancement effect. Note again, that for the heavier adatom, Nb, one is closer to the classical result. It is also noteworthy that the Friedel oscillations inside the bulk jellium are quite similar with and without the adatom.

5. Core states

As we saw in Fig.4, there is a substantial expulsion of the electrostatic field from the region of the adatom. To understand the effect of an external electrostatic field on the adatom, we start from a bare metal surface with an external potential $V_{\text{ext}}^{(M)}(r; F_0)$ due to a surface charge σ_0 producing an asymptotic field $F_0 = 4\pi\sigma_0$. When we bring an atom into this field, it will be polarized, producing an induced field with a potential $V_{\text{ind}}(r)$ which cancels the original field to a large extent in the vicinity of the atom. Because the adatom is in close contact with the metal surface, there will, in addition, be a charge transfer from the atom to the surface involving valence electrons of the adatom. This charge transfer also affects the core-level states, as demonstrated in Fig.5 where we plot the energy eigenvalue of the 1s level of Ti as a function of the nuclear distance from the jellium edge for different field strengths. As discussed in ref.10, the

energy eigenvalues, calculated within the framework of density functional theory, do not directly give the energy to remove an electron from the respective states, however, their distance dependence reflects the variation of the chemical shift. Close to the surface there is a net transfer of electrons from the metal to the adatom generating more repulsion which in turn causes the 1s level of the adatom to be higher than that of the isolated Ti atom. As we move the adatom away from the surface there is eventually some charge draining to the surface creating more attraction so that the 1s level decreases. Even at 4.0 bohr it is still above the 1s level of the Ti^+ ion.

This effect suggests a way to assign a partial charge, q , to the adatom without the inherent arbitrariness connected with the Mulliken population analysis. In lowest order, we set

$$q/e = [E(1s) - E_0(1s)]/[E_+(1s) - E_0(1s)] \quad (15)$$

where $E(1s)$, $E_0(1s)$ and $E_+(1s)$ are the energies of the 1s level of the adatom, the isolated atom and the isolated ion, respectively. This quantity is also plotted in Fig.5 as a function of the adatom position. We note that at 4.0 bohr these partial charges agree with the slopes, $-qF_0$, of the ground-state energy curves.

6. Dipole Moment

Experiments have been devised to extract the dipole moment and the polarisability of a metallic adatom from field emission work function changes⁽¹²⁾. The former quantity can be rigorously defined in our theory as

$$\mu(F_0) = -e \int d^3r \, r [n^{(MA)}(r, F_0) - n^{(M)}(r, F_0) - Z\delta(r-r_0)] \quad (16)$$

where $n^{(MA)}$ and $n^{(M)}$ are the electron number densities with and without the adatom, respectively, and Z is the nuclear charge of the adatom at position r_0 . We note that the total charge in the two situations is identical, i.e. producing an asymptotic field F_0 . This guarantees that the definition (15) of the dipole moment does not depend on the origin chosen.

Looking next at the dependence of the dipole moment, μ , of adsorbed Ti on the adatom position, d , one would expect a linear rise of μ with d , if the charge transfer from the adatom to the metal were independent of the adatom position. However, one finds that the rise is less than linear due to partial re-arrangement of charges as the adatom is pulled away from the surface. Obviously, once one is far enough beyond the hump of the Schottky barrier, the adatom gets ionized and a linear rise in μ should persist up to the point where double ionization becomes possible.

In the experimental literature one parametrizes the dipole moment as

$$\mu(F_0) = \mu(F_0=0) + \alpha F_0 \quad (17)$$

in terms of the asymptotic field F_0 , defining the (field-dependent) polarisability of the surface atom $\alpha(F_0)$, rather than introducing hyperpolarizabilities, gradient terms etc. Values of $\mu(F_0)$ and $\alpha(F_0)$ are given in Table 2. Measured polarisabilities⁽¹²⁾ at field strengths $F_0 < 0.4 \text{ V/\AA}$ decrease monotonically from $11.94 \text{ \AA}^3$ for Ta to $2.74 \text{ \AA}^3$ for Pt. Our numbers for Ti and Nb are, indeed, close to that for Ta.

The field-induced dipole moment of a metal atom at a kink site or on top

of a closed-packed plane has been used by Tsong and Müller⁽¹³⁾ to estimate the local field enhancement

$$\mathbf{F}(\mathbf{r}) = \mathbf{F}_0 + \alpha(\mathbf{F}_0) \frac{3\mathbf{n}(\mathbf{F}_0 \cdot \mathbf{n}) - \mathbf{F}_0}{r^3} \quad (18)$$

Here $\mathbf{F}_0$ is the constant electric field far from the surface and $\mathbf{n}$ is a unit vector in the direction of $\mathbf{r}$. Along a line perpendicular to the jellium surface and through the center of the adatom, the field from (18) is given by

$$F_Z(z) = F_0 \left[1 + \frac{2\alpha(F_0)}{z^3} \right] \quad (19)$$

whereas classical theory gives, from (1-3),

$$F_Z(z) = F_0 \left[1 + \frac{2R^3}{z^3} \right] \quad (20)$$

Tsong and Müller⁽¹³⁾ measured $\mathbf{r}$ in (18) from the nucleus of the adatom, rather than from the center of mass of the charge distribution. This overestimates the field enhancement considerably. We will present a detailed discussion of the effects of field enhancement on field adsorption elsewhere.

7. Conclusions

We have presented self-consistent calculations of the electronic structure of Ti and Nb atoms adsorbed on a jellium metal in the presence of an exter-

nal electric field. We have calculated ground-state energy curves, extracting activation energies for field evaporation and evaporation field strengths, finding good agreement with data for transition metals. Likewise, the calculated dipole moment and polarisability of these metallic adatoms are consistent with experimental values on other metals.

The field enhancement at kink sites, along steps, and above atoms in open surfaces, plays a crucial role in the image formation in the field ion microscope, as demonstrated by the fact that densely packed surfaces cannot be resolved. Our results show that a field enhancement by a factor 1.5 to 2 must be expected 1-2Å above an isolated metal atom. The implications of this effect for field adsorption of rare gases will be explored in a forthcoming paper.

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Table 1: Energy barriers $Q(F_0)$ (in eV). The zero field value, $Q(0)$, is the binding energy.

adatom	F (V/Å)				
	0.0	2.2	2.6	3.0	3.4
Ti	4.3	0.57	0.25	0.09	-
Nb	5.2	1.3	0.64	0.20	0.05

Experimental results⁽¹⁴⁾:

binding energy	4.85 eV for Ti and 7.47 eV for Nb
evaporation field	2.5 V/Å for Ti and 3.5 V/Å for Nb

Table 2: Dipole moment, μ (in Debye) and polarizability, α (in $\text{\AA}^3$), at the equilibrium distance, as a function of field strength.

adatom		F (V/ $\text{\AA}$)			
		2.2	2.6	3.0	3.4
Ti	μ	7.3	10.3	12.5	-
	α	9.9	11.9	12.4	-
Nb	μ	7.3	11.1	13.1	15.0
	α	10.1	12.8	13.1	13.3

Figure Captions

- Fig.1: Potential energy for Nb on jellium with $r_s=3.0$ bohr as a function of nuclear distance, z , from the jellium edge. F_0 in $V/\text{\AA}$.
- Fig.2: Electronic density shift in an electric field for the adatom at the minimum, d , of the potential energy. Left: Ti ($r_s=3.0$ bohr at $d=2.5$ bohr) in $F_0=2.6V/\text{\AA}$. Right: Nb ($r_s=3.0$ bohr at $d=2.75$ bohr) in $F_0=3.0V/\text{\AA}$. Contours $\delta n = 0, \pm 0.0001, \pm 0.002, \pm 0.005, \pm 0.001, \pm 0.002, \pm 0.005$ a.u. Solid (broken) lines non-negative (negative) values. Contours in the core region are omitted.
- Fig.3: External electrostatic potential, upper panels for the same systems as Fig.2; lower panels: classical results. Contour lines $-0.05, -0.02, -0.01, 0.0, 0.03, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$ Ry. Solid (broken) lines non-negative (negative) values.
- Fig.4: Electrostatic field strength along line through the center of the adatom for the same systems as in Fig.2. Curves A and B: without and with the adatom; curve C: classical result.
- Fig.5: $1s$ energy levels and estimated charge, q , for Ti. The levels in the isolated atom and ion are indicated on the right of the left panel.

