Revisiting Local Electric Fields on Close-Packed Metal Surfaces:
Theory versus Experiments

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Abstract. An external electrostatic field of the order of a few tens of a volt per nanometer causes significant changes in the electron density distribution near a metal surface. Because of differing electronic distributions and varying responses of electrons to the applied field for various metals, the resulting local field distribution in the close vicinity of the surface should depend on the electronic properties of the particular metal, even for flat surfaces. Field-free and field-modified electron density distributions for different metal surfaces were calculated using the functional integration method. This approach enables the exchange-correlation effects to be correctly considered and makes it possible to account for the proper field-effect for broad field ranges without using the perturbation theory. The results of calculations are compared with the field-ion microscopic observations.

Introduction

The adsorption of substances that change the reactivity of catalysts (promoters and poisons) modifies the surface by altering the interaction of reactants with the catalyst surface and their mutual interaction. The surface modification can be described by changes of the electron density distribution at and near the surface and can be presented in a simplified view as a modification of the original surface dipole layer [1, 2]. The modified electron density distribution in turn changes the energetics of the adsorption of the reactants and thus the kinetics of the catalyzed surface reaction [1,3,4]. Recently, the influence of a high electrostatic field on the CO oxidation on Pt has been detected which is comparable in scale to the influence caused by the co-adsorption of electropositive adatoms (alkalies or rare earths) [5]. This is understood, since the electrostatic field of the order of a few tens of V/nm can modify the electron density in the surface region to a similar extent as the coadsorption of the electropositive atoms does [6,7]. In contrast to the co-adsorption, the external electrostatic field can be adjusted precisely, by changing the applied voltage, provided the sample can resist the field evaporation that may take place at such high fields [8,9].

Externally applied high electric field may create the electron density distributions which do not exist in the field free conditions, thus surface electronic properties can be “designed” which are not present in nature. Such field-induced modelling has, of course, mainly an academic interest, since it is hardly possible to apply the field of some V/nm in a commercial catalytic process. One can, however, try to create the beneficiary electron density distribution, detected in the high-field experiments, in the field-free conditions, for example by using suitable additives. It is difficult to measure the spatial electron density distribution in high field conditions, nevertheless some evaluation possibilities are provided by field ion microscopy (FIM, [10]), scanning tunnelling microscopy (STM) [8], field ion appearance energy spectroscopy (FIAES, [7,11]), where, for example, local field variations can be estimated, which are unambiguously related to the electron density (via the Poisson equation). It is also possible
to calculate the field-modified surface electron densities and the resulting field distributions \[12, 13\] which can, in turn, be compared with the high-field experiments. For the close-packed fcc (111) surfaces of catalytically important precious metals (Pt, Rh, Pd), the jellium model based calculations appeared to be successful \[14, 15\].

In the paper we propose a new version of the jellium model calculations where the field-free and field-modified electron density distributions are calculated using the functional integration method. The results of calculations are compared with the field-ion microscopic (FIM) observations.

**Calculations**

Most of the published results of field-modified electron density distributions employ the density functional theory (DFT) which mainly uses the local and semi-local approximations (LDA, GGA) \[13, 16\]. Such an approach imposes problems in the description of the van der Waals’ interaction and in the electron density behaviour outside the bulk metal as an implication of many-body effects. We consider the jellium model using the functional integration method \[17\] that allows correct consideration of the exchange-correlation effects and makes possible proper account of the field-effect for broad field ranges without using the perturbation theory. The potential \(V(z)\) necessary for the Schrödinger equation can be described for the case of an external electrostatic field as

\[
V(z) = \frac{\hbar^2}{2m} k_0 z \theta(z) + \frac{\hbar^2}{2m} k_1 z \theta(z),
\]

where the parameter \(k_0\) is chosen via the minimum of the surface energy of the semi-infinite jellium (at zero field) and \(k_1\) reflects the applied field strengths \(F = \frac{\hbar^2}{2m} k_1\).

At low temperatures the electron density can, in turn, be described as \[18\]

\[
n(z) = n_0(z) \exp \left[ -\frac{\lambda_0(z)}{n_0(z)} \sum_{q \neq 0} \overline{g}(q | z, z) \right],
\]

where \(S\) is the surface area, \(q = (q_x, q_y)\), \(q_{x,y} = \frac{2\pi}{\sqrt{S}} m_{x,y}\), \(m_{x,y} = 0, \pm 1, \pm 2, \ldots\), and \(\overline{g}(q | z, z)\) is the effective potential of the electron-electron interaction. For \(n_0\), the electron density in the ideal exchange approximation is used

\[
n_0(z) = \frac{1}{\pi} \sum_{p,\alpha} \phi_\alpha(z) \overline{f}(\epsilon_\alpha(p)),
\]

where \(\phi_\alpha(z)\) and \(\epsilon_\alpha(p)\) are the eigenfunctions and eigenvalues of the Schrödinger equation with the potential \(1\), \(f(\epsilon_\alpha(p))\) – the Fermi function, \(p\) – the electron momentum parallel to the surface, \(p_F = \sqrt{2m\mu/\hbar^2}\) – Fermi momentum, \(\mu\) chemical potential, \(\Theta\) – Heaviside’s function and \(\lambda_0\) is related to \(n_0\) by the equation:

\[
\lambda_0(z) = \frac{\partial}{\partial \mu} n_0(z).
\]

The effective potential of the electron-electron interaction \(g(q | z_1, z_2)\) can be obtained from the integral equation \[17\]

\[
g(q | z_1, z_2) = \nu(q | z_1 - z_2) + \frac{p_{F}}{\pi \hbar^2} \int dz \int dz' \nu(q | z_1 - z) M(q | z, z') g(q | z', z_2),
\]

where

\[
M(q | z, z') = \sum_{k,k'} M_{k,k'}(q, -q) \exp(ikz + ik'z'),
\]

and \(M_{k,k'}(q, -q)\) represents the “density-density” two-particles correlation function \[17\] for the semi-infinite jellium with the particular potential \(V(z)\) of eq. \(1\), \(k = \frac{2\pi}{L} n\), \(n = 0, \pm 1, \pm 2, \ldots\), and

\[
\nu(q | z_1 - z_2) = \frac{2\pi^2}{q} \exp \left( -\frac{q}{2} |z_1 - z_2| \right).
\]

Using the approach proposed in \[17\], equation \(5\) can be analytically solved. The results are for
\( z_1, z_2 \leq 0 \),

\[
g(q \mid z_1, z_2) = \frac{2\pi e^2}{Q_1} \left[ \exp(-Q_1 |z_1 - z_2|) + \frac{Q_1 - Q_2}{Q_1 + Q_2} \exp(Q_1 (z_1 + z_2)) \right],
\]

for \( z_1, z_2 \geq 0 \),

\[
g(q \mid z_1, z_2) = \frac{2\pi e^2}{Q_2} \left[ \exp(-Q_2 |z_1 - z_2|) - \frac{Q_1 - Q_2}{Q_1 + Q_2} \exp(-Q_2 (z_1 + z_2)) \right],
\]

for \( z_1 \leq 0, z_2 \geq 0 \):

\[
g(q \mid z_1, z_2) = \frac{4\pi e^2}{Q_1 + Q_2} \exp(Q_1 z_1 - Q_2 z_2),
\]

and for \( z_1 \geq 0, z_2 \leq 0 \):

\[
g(q \mid z_1, z_2) = \frac{4\pi e^2}{Q_1 + Q_2} \exp(Q_1 z_2 - Q_2 z_1),
\]

Correspondingly. Here \( Q_1 = \sqrt{q^2 + \kappa_{TF}^2 (L(q/2)|p_r| + \Delta(q))} \), \( Q_2 = \sqrt{q^2 - \kappa_{TF}^2 \Delta(q)} \), \( \kappa_{TF} \) is the reciprocal Thomas-Fermi screening radius, \( L(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| \) is the Lindhard-function and \( \Delta(q) = \frac{1}{\rho_F} \left[ \int_0^{\rho_F} \sin(2\gamma \alpha) \left[ 1 - \sqrt{1 - 4 \rho_F^2 - \alpha^2} \right] \left( 1 - 4 \frac{\rho_F^2 - \alpha^2}{q^2} \right) \right] \).

Figure 1 shows the field-free and field modified effective potential of the electron-electron interaction as a function of the electron-electron distance.

![Fig.1: Effective potential of the electron-electron interaction as a function of the electron-electron distance at \( z_1 = z_2 = -10 \) a.u. (1 a.u. = 0.529Å) for \( r_s = 3.0 \) a.u. Jellium edge at \( z=0 \), bulk at \( z < 0 \). Solid line corresponds to zero field, dashed line to the external field of 30V/nm.](image)

The calculated effective potential of the electron-electron interaction is used then for the electron density distributions (eq. 2) which are shown in Fig. 2 for two different bulk electron densities \( n_{\text{bulk}} = \frac{3}{\left(4\pi r_s^3\right)} \), where \( r_s \) is the Wigner-Seitz radius.
The electron density distributions allow the calculation of the electrostatic potential \( \varphi(z) \) by the Poisson equation:

\[
\varphi(z) = \varphi(-\infty) + 4\pi\varepsilon \int_{-\infty}^{z} dz' z'(z'-z) (n(z') - n_+(z')) \tag{12}
\]

where \( n_+(z) = n_{\text{bulk}} \theta(-d-z), \ d > 0 \). The parameter \( d \) can be found self-consistently from the electroneutrality condition \( \int_{-\infty}^{z} d z (n(z) - n_+(z)) = 0 \). The required local electrostatic field strength can be found then as

\[
E(z) = -\frac{d\varphi(z)}{dz} = -4\pi\varepsilon \int_{-\infty}^{z} dz' (n(z') - n_+(z')). \tag{13}
\]

Figure 3 presents the calculated electrostatic field distributions in the close vicinity of the flat metal surface for metals with \( r_s = 2 \) and \( r_s = 3 \) respectively.
Theory versus experiment

To date, it has not been possible to measure the local electrostatic fields of a few tens of V/nm at atomic distances to close-packed metal surfaces. However, it appeared possible to cover a surface of a field emitter tip with an epitaxial layer of another metal and to compare the field ion imaging conditions. In this way the differences in the local electric field close to the surface could be reliably estimated [19, 20]. Here, we apply the “virtual probe-hole approach”, used recently for the analysis of the local brightness fluctuations of the digitized FIM images [21], was applied to the early measurements partially presented in [20]. This makes it possible to evaluate the FIM intensity in arbitrarily chosen regions corresponding to nanosized areas of the tip surface and thus to compare the local field ion emission from the steps of the central (111) plane of the clean and Ag-covered Rh tip, which was hardly achievable at the time of refs. [19,20]. Figure 4 shows the Ne FIM image of the clean surface of a [111] oriented Rh tip and the inset shows the central (111) facet of the same tip epitaxially covered by Ag.

For the same local image, the brightness of Rh- and Ag-atoms located at the first atomic step confining the flat (not-resolved) central facet, the same ion emission rate and thus the same local field can be postulated [22]. The same local brightness of step-site Rh- and Ag-atoms was, however, achieved at different applied voltages (4000 V and 3520 V respectively) i.e. at different externally applied fields \( F_0 \) (35 V/nm and 30.8 V/nm, correspondingly). We define \( F_0 = \beta V \), where \( V \) is the applied voltage and \( \beta \) is the field-to-voltage conversion factor (the details concerning the meaning and determination of \( \beta \) are published elsewhere [11, 20]). Despite of the lower applied field, the local field at Ag step sites is the same for the case of Rh (the same local ion emission). Since the epitaxial Ag-layer on Rh provides the same local geometry, the difference of 4.2 V/nm reflects the different response of Rh and Ag electron systems to the high external field as discussed above.

Of course, the difference in the local fields observed in our experiments is estimated at z-values where the ionization process is localized, that is at the critical distance to the surface \( z_{\text{crit}} \); in addition a field-adsorbed Ne atom is placed between the imaged surface atom (Rh or Ag, correspondingly) and the Ne atom going to be ionized [7,22]. Nevertheless, a semi-quantitative comparison with the result of calculations can be performed, especially taking into account, that the “smooth” atomic steps of the fcc (111) facet (Rh, Ag) are much more closely packed than the “rough” steps of the (110) facet used as the reference in [19,20]. The calculated difference in the local field for \( r_s=2 \) and \( r_s=3 \) \( (r_s \text{ values for Rh and Ag are 1.95 and 3.02, correspondingly [23]), ranges, as follows from Fig. } 3, \text{ between 4.5 and 3.5 V/nm (for } 0<z<2 \text{ a.u.) and is close to the measured 4.2 V/nm. However, one should keep in mind the above-mentioned differences in the “probing point”}. \)
Conclusions

The FIM observations demonstrate that, apart from the atomic geometry of the metal surface, the chemical identity of the surface atoms is essentially contributing to the local field distribution near the metal surface. Present theoretical calculations predicting this effect, include the exchange-correlation effects which are not considered in the known DFT calculations and are in a good agreement with the experimental results. The differences in the field-free spatial electron density distributions for the surfaces of the same crystallography, but different chemical identity, influence such catalytically relevant processes as adsorption, adsorbate dissociation and surface diffusion of adsorbed particles. Additionally they may also contribute to the peculiarities of the STM images of the different metal surfaces with the same atomic structure. The varying response of the electron density distributions to the high electric field influences in turn the FIM image formation and other field induced processes such as field desorption, field evaporation and field-stimulated surface diffusion.

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References