Absorption Model of Hydrogenic Atoms and Ions by Metal Surfaces

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A model of the interaction of thermal atoms and ions with metal surfaces is presented. The model is based on the multi-particle density functional method. This method is applied to describe first the properties of the electron gas on the metal surface and second to analyze the effective potential of the Hydrogenium atom in the vicinity of the metal surface.

Key words: Many-particle density functional method for inhomogeneous electron gas.

In this paper we present a model of the interaction of thermal atoms and ions with metal surfaces. The idea of the method is to calculate the electron density function on the metal surface and the distortion of this function by absorbed atoms and ions. Our calculations are based on the two-particle density functional approach. The Hamiltonian of the system is of the form

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}, \tag{1}$$

where

$$\mathbf{H}_0 = \mathbf{T} + \mathbf{V}_0 + \mathbf{W} \tag{2}$$

is the energy operator of the subsystem consisting of the metal surface and electron gas; $\mathbf{T} = \sum_{i=1}^{N} \left(-\frac{1}{2M} \nabla_i^2 \right)$ is the kinetic energy operator of N electrons; M is the mass of the electron; $\mathbf{V}_0 = \sum_{i=1}^{N} V(\boldsymbol{r}_i)$, where $V(\boldsymbol{r}_i)$ is the interaction potential of the ith electron with the surface, $\boldsymbol{r}_i$ is the radius-vector of the ith electron in a coordinate system with the origin located on the metal surface, $\mathbf{W} = \sum_{i=1}^{N} \sum_{j=1}^{N} W(\boldsymbol{r}_i - \boldsymbol{r}_j)$, $i \neq j$, is the interelectron interaction potential. The system of N electrons is considered in adiabatic approximation, and for the metal surface we use the Jellium model.

The potential $\mathbf{V} = \sum_{i=1}^{N} V(\boldsymbol{r}_i - \boldsymbol{R})$ in (1) is a weak static perturbation created by the field of the proton, and **R** is the proton's radius vector.

The first step of the presented calculations was to find the electron gas density by the condition $\mathbf{V} = 0$. For this the energy functional $\mathscr{E}[n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)]$ of the system was constructed in terms of the two-particle density function $n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$, which is defined as

$$n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{N(N-1)}{2} \cdot \int \psi^*(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)\, \psi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)\, \mathrm{d}^3 r_3 \dots \mathrm{d}^3 r_N,$$

where $\psi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_N)$ is the solution of the Schrödinger-equation of the Hamiltonian (2). Using the two-particle density method, this permits us to take into account two-particle correlations of the system without any exchange-correlation potential. The energy functional is of the form [1]

$$\begin{aligned} \mathscr{E}[n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)] = {} & \mathscr{T}[n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)] \\ & + \frac{2}{N-1} \int (\mathscr{V}(\boldsymbol{r}_1) \\ & + \mathscr{V}(\boldsymbol{r}_2))\, n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2 \\ & + \int \mathscr{W}(\boldsymbol{r}_1 - \boldsymbol{r}_2)\, n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\, \mathrm{d}^3 r_1\, \mathrm{d}^3 r_2, \end{aligned} \tag{3}$$

where the kinetic energy function $\mathscr{T}[n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)]$ is chosen as a gradient expansion which can be found for any N-electron system (electron gas on the metal surface, atoms) in the form

$$\begin{aligned} \mathscr{T}[n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)] = {} & \frac{\pi}{2M(N-1)} \left(\frac{3}{5} \right) (18\pi^4)^{\frac{1}{3}}\, n_2^{\frac{4}{3}}(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ & + \frac{5}{576} (\nabla_2 n_2(\boldsymbol{r}_1, \boldsymbol{r}_2))^2 \\ & + (\nabla_2 n_2(\boldsymbol{r}_1, \boldsymbol{r}_2))^2)\, n_2^{-1}(\boldsymbol{r}_1, \boldsymbol{r}_2) \\ & - \frac{1}{480} (\nabla_1^2 + \nabla_2^2)\, n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)) + \dots . \end{aligned}$$

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The convergency of the given gradient expansion we analyze empirically by using Hooke's Law model applied for the Helium like atom. The electron–nucleus attraction is replaced by an harmonic oscillator potential, but the electron–electron repulsion remains Coulombic [2]. For the Helium atom the Hamiltonian is

$$\mathbf{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \frac{1}{2}k(r_1^2 + r_2^2) + \frac{1}{r_{12}},$$

where k is the oscillator spring constant, r_1 and r_2 are the distances of the electron from the nucleus, and $r_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$. For the particular value $k = \frac{1}{4}$ the solution can be obtained analytically as $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = N_0(1 + \frac{r_{12}}{2})\exp(-\frac{1}{4}(r_1^2 + r_2^2))$ with a normalization constant N_0. Using this function, we construct the two-particle density function $n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = |\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)|^2$ and calculate the terms in the gradient expansion of the kinetic energy functional. The result of this calculation shows that the terms of higher order are small compared to the first one, i.e. $\mathcal{T}[n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)] = 0.645 + 0.037 - 0.003 + \ldots$. The comparison with the calculations of $\mathcal{T}$ in different models [2] in the frame of different one-particle methods shows good agreement with the first order term. The electron density $n(\boldsymbol{r}_1)$ on the metal surface we obtain by the expression

$$n(\boldsymbol{r}_1) = \int n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\mathrm{d}^3 r_2,$$

where the function $n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is calculated by the variational method on the basis of (3). The trial function for this calculation is chosen in the form given in [1]:

$$\begin{aligned} n_2(\boldsymbol{r}_1, \boldsymbol{r}_2) &= C(\phi_1^2(\boldsymbol{r}_1)\phi_2^2(\boldsymbol{r}_2) + \phi_1^2(\boldsymbol{r}_2)\phi_2^2(\boldsymbol{r}_1) \\ &\quad + \alpha\,\phi_1(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2)\phi_2(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2)), \\ \boldsymbol{r}_i &= (x_i, y_i, z_i), \\ \phi_i(\boldsymbol{r}_j) &= \left(1 - \frac{1}{2}\exp(\beta_i z_j)\right)\Theta(-z_j) \\ &\quad + \frac{1}{2}\exp(-\beta_i z_j)\,\Theta(z_j), \quad i, j = 1, 2. \end{aligned} \tag{4}$$

Here β_1 and β_2 are variational parameters, C is a normalization constant, $\alpha = -\frac{3}{2}(\beta_1 + \beta_2)^2(\beta_1^2 + \beta_1\beta_2 + \beta_2^2)^{-1}$. The z-axis is perpendicular to the metal surface.

On the basis (3), the minimization is done for a series of metal surfaces. The values of the variational parameters β_1 and β_2 of the two-particle density function $n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ are given in Table 1. Using the two-particle density function given in (4) with the parameters β_1 and β_2 from Table 1, the works function $\mathcal{F}_e$ is calculated for the same series of metals. The outcomes of these calculations together with the theoretical results in the frame of the one-particle density function according to [3] and the experimental data taken from [4, 5] are presented in Table 2.

Table 1. Variational parameters β_1 and β_2 of the two-particle density function given in (4).

Metal	β_1 [a.u.]	β_2 [a.u.]
Ni	1.750	1.789
Pd	1.451	1.328
Ir	1.740	1.761
W	1.794	1.776
Nb	1.750	1.789
In	1.374	1.474
Zn	1.579	1.509
Cd	1.450	1.321
Cu	1.437	1.344

Table 2. Work function of the electron for several metal surfaces.

Metal	$\mathcal{F}_e$ [eV]			
	pres. calc.	theor. calc. [3]	exp. data [4]	exp. data [5]
Ni	3.81	–	4.50	5.20 ± 0.18
Pd	3.92	–	4.8	5.55 ± 0.1
Ir	5.40	4.02	5.3	5.38 ± 0.38
W	4.47	3.91	4.5	4.72 ± 0.54
Nb	3.81	3.81	3.99	4.3 ± 0.15
In	3.74	3.44	3.8	–
Zn	4.47	3.50	4.24	4.9 (0.001)
Cd	3.76	3.36	4.1	–
Cu	4.41	3.32	4.4	4.65 ± 0.05

The distortion of the electron gas density in the presence of ions due to the weak static potential $\mathcal{V}(\boldsymbol{r}_i - \boldsymbol{R})$ is estimated by a perturbation theory, based on the Lagrange-Euler equation of the form

$$\frac{\delta}{\delta n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)}(\mathcal{E}[n_2] - \mu_2 \int n_2(\boldsymbol{r}_1, \boldsymbol{r}_2)\,\mathrm{d}^3 r_1\,\mathrm{d}^3 r_2)\big|_{n2(\boldsymbol{r}_1, \boldsymbol{r}_2) = n2(gs)(\boldsymbol{r}_1, \boldsymbol{r}_2)} = 0, \tag{5}$$

where μ_2 is the Lagrange constant. In the frame of the given perturbation method we consider the family of operators

$$\mathbf{H}_\lambda = \mathbf{H}_0 + \lambda\mathbf{V},$$

where $\lambda \in [0, 1]$ is a dimensionless parameter. The eigenfunctions, density functions $n_2^{(\lambda)}$, the energy of the ground state $\mathcal{E}_\lambda$ and the Lagrange constant $\mu_2^{(\lambda)}$ corresponding to the Hamiltonian $\mathbf{H}_\lambda$ may be expanded by the parameter λ:

$$\begin{aligned} n_2^{(\lambda)}(\mathbf{r}_1,\mathbf{r}_2) &= n_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2) + \lambda\, n_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2) \\ &\quad + \lambda^2 n_2^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + \dots, \\ \mathscr{E}_\lambda &= \mathscr{E}^{(0)} + \lambda\,\mathscr{E}^{(1)} + \lambda^2 \mathscr{E}^{(2)} + \dots, \\ \mu_2^{(\lambda)} &= \mu_2^{(0)} + \lambda\,\mu_2^{(1)} + \lambda^2 \mu_2^{(2)} + \dots . \end{aligned} \tag{6}$$

Here $n_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2)$, $\mathscr{E}^{(0)}$, and $\mu_2^{(0)}$ correspond to the unperturbed Hamiltonian $\mathbf{H}_0$. Inserting the expressions (6) into (5), the chain of equations for $n_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2)$, $n_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2)$,... and $\mu_2^{(0)}$, $\mu_2^{(1)}$,... is obtained.

In the first approximation we need only the first and second equation of the chain. The first equation is the Lagrange-Euler equation for the unperturbed system. The second equation may be solved with respect to the function $n_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2)$ if the density function $n_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2)$ and the kinetic energy functional are known. The present method is used for the analysis of the distortion of the electron density function by Hydrogen atoms and ions. We define the energy of the proton interaction with the metal surface in the first approximation of the perturbation theory by the expression

$$\begin{aligned} \mathscr{E}_{\text{int}}(\mathbf{R}) &= \mathscr{V}_0(\mathbf{R}) - \mathscr{V}_1(\mathbf{R}) - \mathscr{V}_2(\mathbf{R}), \\ \mathscr{V}_1(\mathbf{R}) &= \frac{2}{N-1}\int \frac{n_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{R}-\mathbf{r}_1|}\,\mathrm{d}^3 r_1\,\mathrm{d}^3 r_2, \\ \mathscr{V}_2(\mathbf{R}) &= \frac{1}{N-1}\int \frac{n_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2)}{|\mathbf{R}-\mathbf{r}_1|}\,\mathrm{d}^3 r_1\,\mathrm{d}^3 r_2, \end{aligned} \tag{7}$$

where $n_2^{(0)}$ and $n_2^{(1)}$ are the zeroth and the first term of the expansion of $n_2(\mathbf{r}_1,\mathbf{r}_2)$ into the perturbation's series.

The numerical calculations on the basis of (7) shown that $\mathscr{E}_{\text{int}}$ has a minimum which corresponds to the adsorption energy $\mathscr{E}_{\text{p}}$ of hydrogenic ions at a distance $R_z = Z_0$ from the metal surface. The calculations of the proton interaction energy with the Wolfram metal surface and the electron gas with respect to (7) are presented in Figure 1. Using

$$n_1^{(1)}(z,\mathbf{R}) = \int n_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\,\mathrm{d}^3 r_2,$$

$\mathbf{r}_1 = (0,0,z)$, $\mathbf{R} = (\mathbf{u}, R_z)$, $R_z = Z_0$, $\mathbf{u} = (R_x, R_y)$ and $u = |\mathbf{u}|$, the corrections due to the proton distortion are calculated. The result of this calculation is shown in Fig. 2 for different u. The adsorption energy $\mathscr{E}_{\text{a}}$ of hydrogenic atoms by the metal surface is determined from the expression

$$\mathscr{E}_{\text{a}} = \mathscr{E}_{\text{p}} + \mathscr{F}_{\text{e}} - \mathscr{I}_{\text{a}}, \tag{8}$$

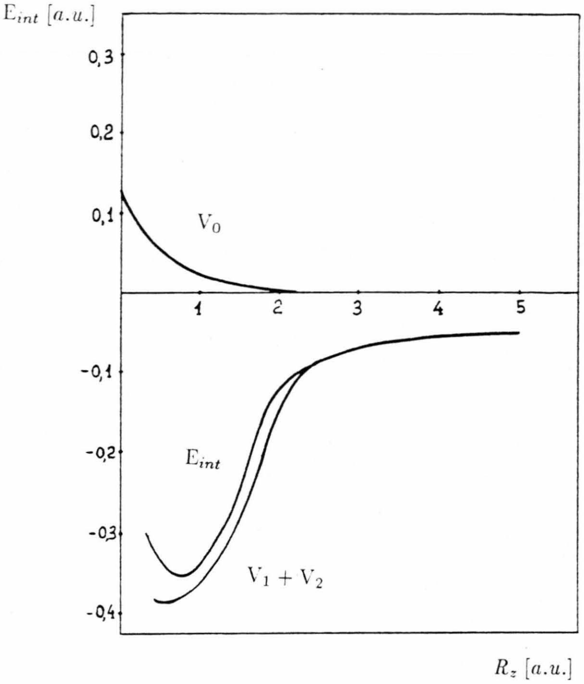

Fig. 1. Interaction energy of protons with the Wolfram surface calculated according to (7).

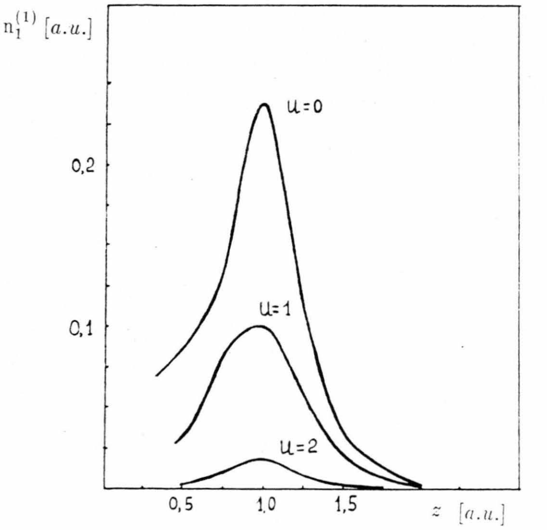

Fig. 2. Correlation of the electron density function $n_1^{(1)}(\mathbf{r}_1,\mathbf{R})$ due to the protein position $\mathbf{R} = (\mathbf{u}, R_z)$, $R_z = Z_0$, on the Wolfram metal surface for $R_z = 1$ a.u. and $\frac{u}{[\text{a.u.}]} = 0, 1, 2, \dots$.

Table 3. Adsorption energy $\mathcal{E}_p$ for protons and $\mathcal{E}_a$ for the hydrogenic atom on the metal surface.

Metal	W(100)	W(110)	Pd(110)	Ir	CuIII	Ni
$n[10^{-3}$ a.u.$]$[a]	56.2	56.2	12.9	84.2	12.6	40.0
$\mathcal{E}_p$[eV]. pres. calc.	10.1	10.1	8.72	9.8	8.72	9.9
exp. data [6]	11.3	10.3	9.09	9.4	10.14	8.92
calc. from [7]	9	9	–	–	–	–
$\mathcal{E}_a$ [eV] pres. calc.	2.2	2.2	0.67	1.5	0.1	1.45
exp. data [6]	3.4	3.0	0.52	1.17	1.21	0.47
calc. from [7]	0.7	0.7	–	–	–	–
Z_0 [a.u.] pres. calc.	1.01	10.1	1.28	1.14	1.27	1.01
exp. data [6]	–	–	1.97	–	–	–
calc. from [7]	1.08	1.08	–	–	–	–

[a] Meanvalue of the positive charge in atomic units.

where $\mathcal{F}_e$ is the electron work function and $\mathcal{I}_a$ the ionization potential of the hydrogenic atom. The results of the numerical calculations for several metal surfaces are presented in Table 3, together with the experimental data from [6] and the results of calculations in the one-particle density approach [7].

Table 4. Ground state and first vibrational state energy of protons adsorbed on the metal surface.

Metal	W	Cu(100)	Ni(100)	Ir	Pd(100)
$\mathcal{E}_{v,\text{theor.}}$ [meV]					
$l=0$	84	59	81	78	58
$l=1$	252	177	243	234	174
$\mathcal{E}_{p,\text{exp.}}$ [meV] [8]					
$l=0$	–	24.9	78	–	63
$l=1$	–	–	93	–	–

The effective potential of the proton in the vicinity of the metal surface around its minimum can be considered as an oscillator potential. Then the vibrational energy of the proton may be represented in the form

$$\mathcal{E}_v(l) = \left(\frac{1}{M_p}\,\frac{d^3\,\mathcal{E}_{\text{int}}(\mathbf{R})}{dZ^2}\right)^{\frac{1}{2}}\Bigg|_{Z=Z_0}\left(l+\frac{1}{2}\right) \qquad (9)$$

where M_p is the mass of the proton, $l=0,1,2,\ldots$. The vibrational energy $\mathcal{E}_v$ of protons adsorbed by metal surfaces is also calculated by using (9). The results are presented in Table 4, together with experimental data [8] for the ground ($l=0$) and the first ($l=1$) vibrational states.

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