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ON HYDROGEN GHEMISORPTION ON SIMPLE METALS

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1. INTRODUCTION

One of the most interesting problems in solid state physics is a satisfactory description of the chemisorption of a light gas atom on metal surfaces. The great complexity of actual systems has prompted a study of model Hamiltonians, one of which, the Anderson model, is widely used. Usually, using the Anderson Hamiltonian for the explanation of the experimental data of the atomic hydrogen chemisorption on metal surfaces, two parameters of this model are fitted from experiment.

The first parameter is the Coulomb intra-atomic interaction for the adatom, U , and the second is the hybridization parameter β built up from the matrix elements $V_{\alpha\vec{k}}$ which determine the electron hopping between the adatom and the substrate metal. The renormalization of the Coulomb repulsion may be explained by the inclusion into consideration of the image potential. It is well known that the electron-surface interaction far outside the surface is described by the image form with the reference plane shifted outwards from the edge of the jellium background [1], but there are large deviations as the electron approaches the surface, and within a few atomic units of the surface the corrections can be comparable to the image term [2]. Moreover, the location of the effective image plane relative to the jellium adge varies with the density of conduction electrons and, for example, for metals like Al (small r_s) one has a stronger image force on a charge at the same distance from the jellium edge [1]. All the above considerations concern static charge but this problem is known to have a dynamical nature, too. For example, the image-plane location is a function of frequency and moves closer to their jellium edge for moving charges [2]. Note that for the experimental values of the distance between the adatom and metal surfaces this image effect can lead to considerable reduction of the Coulomb repulsion U.

Especially difficult problem in the Anderson model is the estimation of the matrix element $V_{\alpha\vec{k}}$ .In order to do this, one has to know the wave functions and the nature of the interaction between the adatom and the metal surface. In addition, as was shown in Ref. [3], the hybridization of the substrate and adatom electron states can be influenced by the partial occupation of the adsorbate resonances and in general case can be dependent on the adatom electron spin.

In this paper we present numerical results for some characteristics of the hydrogen chemisorption on a free-electron - like substrate modelled by the semi-infinite jellium system in the framework of the Hamiltonian introduced in Ref.[3]. In the absence of a realistic value of U we decided to examine some chemisorption characteristics for a wide variety of the on-adatom Coulomb repulsion values. The matrix elements $V_{\alpha\vec{k}}$, $V_{AAA\vec{k}}$ inherent in the model are calculated from first principles and all the calculations were done in the Hartree-Fock approximation in a self-consistent way. Usually, this type of investigations is performed in the framework of the local density functional formalism [4]; nevertheless, it should be mentioned that despite the achievements of this approach, some characteristics of the chemisorption process cannot be determined [5].

This paper is organized as follows. In the next section we discuss the Hamiltonian describing the chemisorption process and its parameters from a microscopic point of view. We present the formulae for evaluation of the matrix elements and the basic relations for calculations of the chemisorption characteristics calculated in a self-consistent Hartree-Fock approximation. The last section 3 is devoted to the presentation of the numerical calculations for the chemisorption energy, the charge transfer between the adatom and the substrate and for other characteristics and discussion.

2. HARTREE-FOCK DESCRIPTION OF THE CHEMISORPTION

Following the method represented in Ref.[3] we can present the Hamiltonian for the adatom-metal substrate system in the form

$$H = \sum_{k\sigma} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + \sum_{\sigma} E_A\, n_{A\sigma} + U\, n_{A\sigma} n_{A-\sigma} + \sum_{k\sigma} \Big[\big(V_{A\vec{k}} - n_{A-\sigma} V_{AAA\vec{k}} \big)\, a^{+}_{A\sigma} a_{\vec{k}\sigma} + \text{H.c.} \Big] + H_{\text{rest.}} + U_{\circ} \quad , \tag{1}$$

where

$$V_{AAA\vec{k}} = - \int d\vec{x}\, d\vec{y}\; \varphi^{*}_{A}(x) \varphi^{*}_{A}(\vec{y}) \varphi_{A}(\vec{y}) \varphi_{\vec{k}}(\vec{x})\; V(\vec{x}-\vec{y}) \quad ,$$

$$V_{A\vec{k}} = - \int d\vec{x}\; V(\vec{R}_A - \vec{x})\; \varphi^{*}_{A}(\vec{x}) \varphi_{\vec{k}}(\vec{x}) \tag{2}$$

and $V(\vec{x} - \vec{y})$ - describes the the electrostatic Coulomb interaction between unit charges (electrons) placed at the positions $\vec{x}$ and $\vec{y}$, and other parameters entering into Eq.(1), i.e., $\epsilon_{\vec{k}}$, E_A and U have their usual meaning [3,6]. The term $H_{\text{rest.}}$ involves the interactions which are not usually considered in the simple chemisorption models and generalizes the Anderson model. Here we do not consider these terms and refer the reader to Ref. [3] for a more detailed discussion. So, we confine ourselves to the model in which together with the standard interactions present in the Anderson model [6], also the effects connected with the influence of the adatom orbital occupation on the charge transfer between an adatom and a metal substrate are included. If we use an explicit form for the Coulomb interaction and for the hydrogen 1S -electron wave function, then it can be shown [3] that for the seperation between the adatom and the substrate surface much greater than the atomic length one obtains $V_{AAA\vec{k}} \simeq V_{A\vec{k}}$. In that case the charge transfer from the substrate to the adatom is suppressed for Hamiltonian (1) in comparison with the predictions obtained within the Anderson model [3]. When the adatom is located near the surface, then we can approximate the matrix element $V_{AAA\vec{k}}$ as $\alpha\, V_{A\vec{k}}$, $\alpha \le 1.0$, i.e., with the adatom moving towards the surface the parameter α decreases. In the next section, we investigate more precisely this kind of approximation. The Hartree-Fock approximation for the system described by Eq.(1) is equivalent to considering of the approximate Hamiltonian

$$H = \sum_{k\sigma} \epsilon_{\vec{k}}\, n_{\vec{k}\sigma} + \sum_{\sigma} E_{\sigma}\, n_{A\sigma} + \sum_{k\sigma} \Big[\big(V_{A\vec{k}} - n_{A-\sigma} V_{AAA\vec{k}} \big)\, a^{+}_{A\sigma} a_{\vec{k}\sigma} + \text{H.c.} \Big] + C \quad , \tag{3}$$

where

$$E_\sigma = E_A + U \langle n_{A-\sigma} \rangle - \sum_k [V_{AAA\vec{k}} \langle a^+_{A-\sigma} a_{\vec{k}-\sigma} \rangle + \mathrm{H.c.}] , \tag{4}$$

$$C = - U \langle n_{A\uparrow} \rangle \langle n_{A\downarrow} \rangle + \sum_{k\sigma} [V_{AAA\vec{k}} \langle n_{A-\sigma} \rangle \langle a^+_{A\sigma} a_{\vec{k}\sigma} \rangle + \mathrm{H.c.}].$$

Note that in contrast with the Hartree-Fock description of the standard Anderson model here the quantity

$$V_{A\vec{k}} - V_{AAA\vec{k}} \langle n_{A-\sigma} \rangle ,$$

which determines the electron hopping between the adatom and the substrate, depends on the occupation of the adatom orbital.

Using the Green function technique [7] one can obtain the following set of nonlinear integral equations for an average number of electrons $\langle n_{A\sigma} \rangle$ on the adatom orbital (for a temperature $\theta = 0\,^\circ\mathrm{K}$):

$$\langle n_{A\sigma} \rangle = \left[1 - \frac{d\, S^{-\sigma}(\omega)}{d\, \omega} \Big|_{\omega = E^\sigma_L} \right]^{-1} - \frac{1}{\pi} \int_{\varepsilon_0}^{\varepsilon_F} d\omega \, \frac{\mathrm{Im}\, S^{-\sigma}(\omega)}{[M^\sigma(\omega)]^2 + [\mathrm{Im}\, S^{-\sigma}(\omega)]^2} , \tag{5}$$

where E^σ_L is a solution of the following equation:

$$M^\sigma(\omega) = \omega - E_A - U \langle n_{A-\sigma} \rangle + R^{-\sigma} - \mathrm{Re}\, S^{-\sigma}(\omega) = 0 \tag{6}$$

and

$$\begin{aligned} R^\sigma = {} & 2 \left(\mathrm{Re}\, F^{-\sigma}(\omega) \left[1 - \frac{d\, S^{-\sigma}(\omega)}{d\, \omega} \right]^{-1} \right) \Big|_{\omega = E^\sigma_L} - \\ & - \frac{2}{\pi} \int_{\varepsilon_0}^{\varepsilon_F} d\omega \, \frac{1}{[M^\sigma(\omega)]^2 + [\mathrm{Im}\, S^{-\sigma}(\omega)]^2} \times \\ & \times \Big\{ [\omega - E_A - U \langle n_{A-\sigma} \rangle + R^{-\sigma} - \mathrm{Re}\, S^{-\sigma}(\omega)] \, \mathrm{Im}\, F^{-\sigma}(\omega) + \\ & + \mathrm{Im}\, S^{-\sigma}(\omega) \, \mathrm{Re}\, F^{-\sigma}(\omega) \Big\} , \end{aligned} \tag{7}$$

$$\begin{aligned} F^\sigma(\omega) &= \sum_k \frac{V_{AAA\vec{k}} (V_{A\vec{k}} - V_{AAA\vec{k}} \langle n_{A\sigma} \rangle)}{E^+ - \varepsilon_{\vec{k}}} , \\ S^\sigma(\omega) &= \sum_k \frac{(V_{A\vec{k}} - V_{AAA\vec{k}} \langle n_{A\sigma} \rangle)^2}{E^+ - \varepsilon_{\vec{k}}} . \end{aligned} \tag{8}$$

In formulae (5) and (7) the first terms exist only when the localized states exist below the substrate energy band. In an analogous way to that in Refs. [3,6], one can obtain expressions for the chemisorption energy ΔE and the adatom charge q

$$\begin{aligned} \Delta E = {} & \sum_\sigma \left(E^\sigma_L + \frac{1}{\pi} \int_{\varepsilon_0}^{\varepsilon_F} d\omega \, \tan^{-1} \left[\frac{\mathrm{Im}\, S^{-\sigma}(\omega)}{M^\sigma(\omega)} \right] \right) + \\ & + E_A - U \langle n_{A\uparrow} \rangle \langle n_{A\downarrow} \rangle + 2 \sum_\sigma \langle n_{A-\sigma} \rangle R^\sigma , \\ q = {} & e (1 - \langle n_{A\uparrow} \rangle - \langle n_{A\downarrow} \rangle) , \end{aligned} \tag{9}$$

where ε_0 is the bottom of the energy band which is present in forming the chemisorption bond and E^σ_L is the energy of the localized electron states ($E^\sigma_L < \varepsilon_0$). In Eq.(9) the energy zero is placed at ε_- . In the absence of the occupied localized state we discard the term E^σ_L and take $-\pi$ < arctan < 0 (if an occupied localized state exists, then 0 < arctan < π).

3. NUMERICAL RESULTS AND CONCLUSIONS

The above presented theory is adopted to hydrogen chemisorption on free-electron-like substrates described by a jellium model. The first problem we have to solve is the calculation of the matrix elements $V_{a\vec{k}}$ and $V_{AAA\vec{k}}$ (see Eq.(2)). For this purpose, we use the hydrogen 1S - electron wave-functions and the metal states are taken to be free electron states, plane waves inside the metal and exponentially damped waves outside the metal in the direction normal to the surface

$$\psi_{\vec{k}}(z) = \frac{1}{\sqrt{V}} \exp (i \vec{K} \vec{R}) \, \psi_{k_z}(z) . \tag{10}$$

Here V is a volume of the system and $(\vec{K}, k_z) = \vec{k}$, $(\vec{R}, z) = \vec{x}$, where the "z" direction is normal to the surface. The ψ_{k_z} depends on the model of the surface chosen. We have adopted a finite-barrier potential model to describe the surface with the barrier of height $V_\circ$ taken at $z = z_\circ$ (in a further consideration we put $z_\circ = 0$), so, we have (see, e.g. [8])

$$\psi_{k_z}(z) = \begin{cases} \cos\left[\, k_z(z - z_\circ) + \delta(k_z) \,\right] & \text{for } z < z_\circ \,; \\ \dfrac{k_z}{k_\circ} \exp\left[\, -q_z(z - z_\circ) \,\right] & \text{for } z > z_\circ \,, \end{cases} \tag{11}$$

where the phase shift is given by $\delta(\omega) = -\dfrac{q_z}{k_z}$ and

$$k_\circ^2 = \frac{2m}{h} V_\circ \;, \quad q_z^2 = k_\circ^2 - k_z^2 \,.$$

The explicit evaluation of the matrix elements $V_{A\vec{k}}$ and $V_{AAA\vec{k}}$ is given in Appendix. As a next step, we need to calculate the function $F^\sigma(\omega)$ and $S^\sigma(\omega)$ defined in Eq.(8). We first calculate the imaginary part and then use the Kramers-Kronig relation to obtain the real parts. For $F^\sigma(\omega)$ we have (one can proceed in analogous way for $F^\sigma(\omega)$)

$$\begin{aligned} \mathrm{Im}\, F^\sigma(\omega) = {} & -\pi \sum_{k} V_{A\vec{k}} \left(V_{A\vec{k}} - V_{AAA\vec{k}} \langle n_{A-\sigma} \rangle \right) \delta(\omega - \varepsilon_{\vec{k}}) - \\ & - \frac{2m}{8\pi h^2} \int dk_z \; \bar{V}_{AAA\vec{k}} \left(\frac{2m\omega}{h^2} - k_z^2,\, k_z \right) \Big[\bar{V}_{A\vec{k}} \left(\frac{2m\omega}{h^2} - k_z^2,\, k_z \right) - \\ & - \bar{V}_{AAA\vec{k}} \left(\frac{2m\omega}{h^2} - k_z^2,\, k_z \right) \langle n_{A\sigma} \rangle \Big] , \end{aligned} \tag{12}$$

where for $\varepsilon_{\vec{k}}$ we have used the free-electron energy dispersion law and $\bar{V}_{A\vec{k}} = \sqrt{V}\, V_{A\vec{k}}$ (the same for $\bar{V}_{AAA\vec{k}}$).

The set of equations (5-8,12) determines the self-consistent treatment of the hydrogen adatom chemisorption on the free-electron-like substrates in the Hartree-Fock approximation.

In the next step we present the results of the numerical calculations. In figures 1-2 we depicted the matrix elements $V_{A\vec{k}}$ and $V_{AAA\vec{k}}$ as functions of the adatom-surface distance $|\vec{R}_A| = R_A$ and k_z (the perpendicular to the surface part of wave vector $\vec{k}$ for $|\vec{k}| = k_F$). We can see, that the matrix elements $V_{A\vec{k}}$ and $V_{AAA\vec{k}}$ show the similar behaviour as function of k_z at fixed energy and different distances R_A. So, its ratio α, figure 3, slightly depends on k_z and approximation $V_{AAA\vec{k}} \simeq \alpha V_{A\vec{k}}$ introduced in Ref.[3] works very good. In figure 4, we show the dependence of the matrix elements $V_{A\vec{k}}$ and $V_{AAA\vec{k}}$ on distance R_A at different values k_z. This dependences show similar minimum at certain values of R_A. This causes the increase of the obsorption tendency in the behaviour of the chemisorption energy versus R_A in the model described by Hamiltonian (3), comparing with the usual Anderson model ($V_{AAA\vec{k}} = 0$). This fact can be explained as the minimum in the distance dependence of the matrix element $V_{A\vec{k}}$ is compensated by the similar distance dependence of $V_{AAA\vec{k}}$ in function $S^\sigma(\omega)$. Comparing the experimental chemisorption energy with that one represented in figure 5, we find the effective value of the intraadatom Coulomb interaction parameter U approximately equal 7-8 eV. In figure 6 we present the distance dependence of the occupation number of the surface impurity resonance. The jump from the occupation number 1 to 2 (i.e., from nearly neutral to almost charged state of hydrogen's adatom) with decreasing values of U corresponds to the case when the impurity resonance level accrosses the Fermi level of the substrate

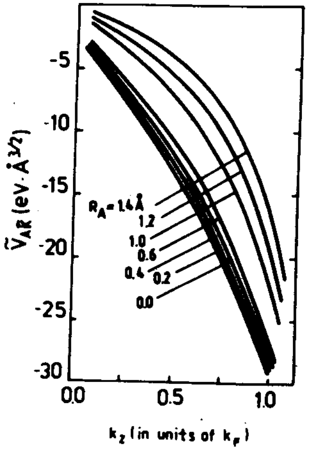

Fig. 1. The dependence of the matrix element $V_{A\vec{k}}$ on k (perpendicular to the surface part of the wave vector $\vec{k}$) for $|\vec{k}| = k_F$ for different values of R_A (distance of the adatom from the surface).

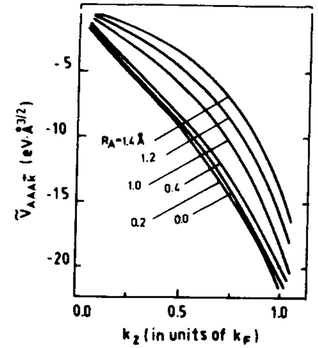

Fig. 2. The same as in figure 1 except for $V_{AAA\vec{k}}$.

electron band. In the last figure (7) we depicted the chemisorption function, $S^{\sigma}(\omega)$, used in our calculations.

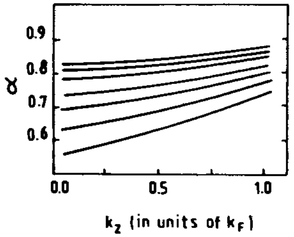

Fig.3. The dependence of the parameter α (see text) on the k_F for $|\vec{k}|=k_z$ for different values of R_A equal 1.4, 1.2, 1.0, 0.6, 0.4, 0.2 and 0.0 A° for curves from the top to botton of this figure.

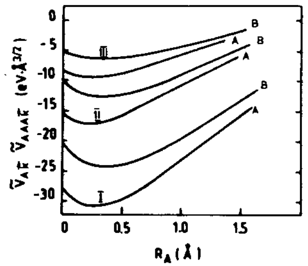

Fig. 4. The dependence of the matrix elements $V_{A\vec{k}}$ - curves A and $V_{AAA\vec{k}}$ - curves B on the adatom's distance R_A from the surface for $\omega = \varepsilon_F$ and for different values of the k_z :

$I - k_z = k_F \simeq 1.8\ A^{\circ -1}$,

$II - k_z = 1.45\ A^{\circ -1}$,

$III - k_z = 1.0\ A^{\circ -1}$.

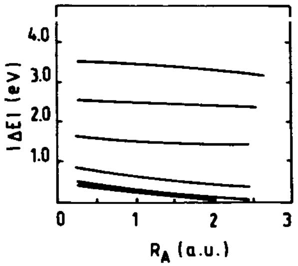

Fig. 5. The chemisorption energy ΔE for different values of the Coulomb interaction U equal to 12.9 eV - the lower curve and 10, 9, 8, 7 and 6 eV for next curves, respectively.

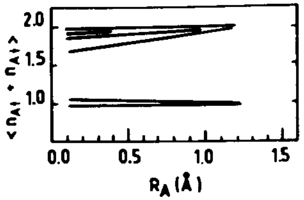

Fig. 6. The total electron charge on the hydrogen adatom vs. R_A for different values of U equal 12.9, 10, 9, 8, 7 and 6 eV for curves from bottom to the top of figure, respectively.

In conclusion, comparing our results with the calculations of other authors done within the LDF (the Local Density Functional Method) [1], we obtained the prefering of the hydrogen obsorption on the simple metal substrates and more slightly distance dependence of the chemisorption energy.

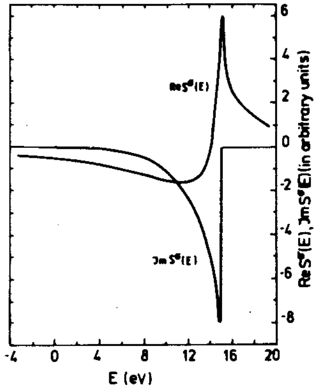

Fig. 7. The real and imaginary parts of the chemisorption function $S^{\sigma}(\omega)$ for some values of $\langle n_{A\sigma}\rangle$.

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APPENDIX

In this section we give some details of calculations of the matrix elements $V_{A\vec{k}}$ and $V_{AAA\vec{k}}$. Using the substrate electron wave function in the form (10) and hydrogen 1S - electron wave function as

$$\Phi_A(\vec{x}) = \Phi(\vec{R}_A - \vec{x}) = \frac{1}{\sqrt{\pi a^3}} \exp [-| \vec{R}_A - \vec{x} | / a] , \quad a = \frac{h^2}{me^2}$$

we can write

$$V_{AAA\vec{k}} = V_{A\vec{k}} - \Delta_{A\vec{k}} ,$$

$$V_{A\vec{k}} = -\frac{e^2}{\sqrt{\pi a^3 V}} \int dz\, \psi_{k_z}(z) \iint d\vec{R} \exp (i\vec{k}\vec{R}) \times$$

$$\times \exp [-| \vec{R}_A - \vec{x} | / a] \, | \vec{R}_A - \vec{x} |^{-1} ,$$

$$\Delta_{A\vec{k}} = -\frac{e^2}{\sqrt{\pi a^3 V}} \int dz\, \psi_{k_z}(z) \iint d\vec{R}\, exp\,(\, i\vec{k}\vec{R}\,) \times$$
$$\times \left(\frac{1}{a} + \frac{1}{|\,\vec{R}_A - \vec{x}\,|} \right) exp\,[\, -3|\,\vec{R}_A - \vec{x}\,|\,/\,a\,]\ .$$

In order to obtain the above written formulae in the form more appropriate to numerical calculations we have to calculate in an analytical form the integrals

$$J_1 = \iint_{-\infty}^{\infty} d\vec{R}\, exp\,(\, i\vec{k}\vec{R}\,) \times \frac{1}{r}\, exp\,(\, -r/a\,) \equiv J_1(z') \quad ,$$

$$J_2 = \iint_{-\infty}^{\infty} d\vec{R}\, exp\,(\, i\vec{k}\vec{R}\,) \times \left(\frac{1}{r} + \frac{1}{a} \right) exp\,(-3r/a\,) \equiv J_2(z') \quad ,$$

$$|\,\vec{R}_A - \vec{x}\,| = |\,(00R_A) - (xyz)\,| = |\,(000) - (x,y,z')\,| = r\ .$$

Using the following identities [8]

$$\frac{1}{r}\, exp\,(\, -\alpha\, r\,) = \frac{1}{2\pi^2} \iiint d\vec{\beta}\, \frac{exp\,(\, i\vec{\beta}\,\vec{r}\,)}{\alpha^2 + \beta^2} \quad ;$$

$$exp\,(\, -\alpha\, r\,) = \frac{1}{2\pi^2} \iiint d\vec{\beta}\, \alpha\, \frac{exp\,(\, i\vec{\beta}\,\vec{r}\,)}{(\, \alpha^2 + \beta^2\,)^2}$$

we can obtain for J_1 and J_2 the formulae

$$J_1 = 2 \int d\beta_z\, \frac{exp\,(\, i\beta_z z\,)}{F^2 + \beta_z^2} \quad ,$$

$$J_2 = 2 \int d\beta_z\, \frac{exp\,(\, i\beta_z z\,)}{G^2 + \beta_z^2} + \frac{6}{a^2} \int d\beta_z\, \frac{exp\,(\, i\beta_z z\,)}{(\, G^2 + \beta_z^2\,)^2} \quad ,$$

where $F^2 = a^2 + K^2$, $G^2 = 9a^{-2} + K^2$.

The β_z integral can be done in the complex plane by choosing a contour along the real axis from $-\infty$ to ∞ and closing it with a semi-circle in the upper or lower half-plane for convergence (see also, e.g. [8]). Performing the calculations we obtain

$$J_1 = \frac{2\pi\, exp\,(\, -F\, |z|\,)}{F} ,$$

$$J_2 = \frac{2\pi}{G}\, exp\,(\, -G\, |z|\,) + \frac{3\pi}{G^2 a^2} \left(\, |z| + \frac{1}{G}\,\right) exp\,(\, -G\, |z|\,)\ .$$

As a result, we have for the matrix elements $V_{A\vec{k}}$ and $V_{AAA\vec{k}}$ the formulae

$$V_{A\vec{k}} = -\frac{e^2}{\sqrt{\pi a^3 V}} \int dz\, \psi_{k_z}(z)\, J_1(\, z - |\vec{R}_A|\,)\ ,$$

$$V_{AAA\vec{k}} = V_{A\vec{k}} - \frac{e^2}{\sqrt{\pi a^3 V}} \int dz\, \psi_{k_z}(z)\, J_2(\, z - |\vec{R}_A|\,)\ .$$

Finally, using for $\psi_{k_z}(z)$ formulae (11) we obtain

$$V_{A\vec{k}} = -\frac{2\sqrt{\pi}\, e^2}{\sqrt{a^3 V}}\, \frac{1}{F}\, \frac{k_z}{k_0} \Big[\, exp\,(\, -F\, |\vec{R}_A|\,) \left(\frac{F - q_z}{F^2 + k_z^2} - \frac{1}{F - q_z} \right) +$$
$$+ exp\,(\, -q_z |\vec{R}_A|\,)\, \frac{2F}{F^2 - q_z^2} \Big] \quad ,$$

$$V_{AAA\vec{k}} = V_{A\vec{k}} - \frac{2\sqrt{\pi}\, e^2}{\sqrt{a^3 V}}\, \frac{1}{G}\, \frac{k_z}{k_0} \Big[\, exp\,(\, -q_z |\vec{R}_A|\,)\, \frac{2G}{G^2 - q_z^2} +$$
$$+ exp\,(\, -G\, |\vec{R}_A|\,) \left(\frac{G - q_z}{G^2 + k_z^2} - \frac{1}{G - q_z} \right) \Big] -$$
$$- \frac{3\sqrt{\pi}\, e^2}{a^2\sqrt{a^3 V}}\, \frac{1}{G^2}\, \frac{k_z}{k_0} \Big(\, exp\,(\, -q_z |\vec{R}_A|\,)\, \frac{4G^2}{(\, G^2 - q_z^2\,)^2} + exp\,(\, -G\, |\vec{R}_A|\,) \times$$
$$\times \Big[-\frac{2\, G - q_z}{G\,(\, G - q_z\,)^2} + |\vec{R}_A|\,(\, G - q_z\,) \left[\frac{1}{G^2 + k_z^2} - \frac{1}{(\, G - q_z\,)^2} \right] +$$
$$+ \frac{1}{G^2 + k_z^2} \left[\frac{G - q_z}{G} + \frac{G^2 - k_z^2 - 2q_z G}{G^2 + k_z^2} \right] \Big] \Big)\ .$$

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Таранко Е. и др. E17-88-665
О хемосорбции водорода на простых металлах

В рамках ранее предложенного микроскопического подхода, учитывающего влияние частичного заполнения примесной орбитали адатома на гибридизацию, рассмотрена атомная хемосорбция водорода на подложку простого металла. Матричные элементы, входящие в гамильтониан, рассчитываются из первых принципов при использовании 1S-орбитали атома водорода и волновых функций электронов в подложке типа желе. Эффекты экранирования заряда учитываются феноменологически за счет переопределения соответствующим образом кулоновского взаимодействия. Самосогласованные хартри-фоковские расчеты показывают предпочтение абсорбции по сравнению с адсорбцией для водорода на подложке простого металла, получаемой в рамках метода функционала плотности.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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On Hydrogen Chemisorption on Simple Metals

A theoretical study of the single hydrogen adatom chemisorption on free-electron-like metal surfaces is performed using an earlier published microscopic approach which includes the possibility of an influence of the adatom orbital occupancy on the hybridization of the adatom and substrate electron wave functions. The matrix elements inherent to the model are calculated from first principles using a free-electron wave functions for describing the substrate metal and treating the 1S-orbital of the adatom as an auxiliary orbital. The effect of the screening charge is considered phenomologically in terms of an effective on adatom Coulomb integral. The self-consistent Hartree-Fock calculations show a much more prefering of the hydrogen absorption rather than adsorption and more slightly adatom-substrates surface distance dependence of the chemisorption energy comparing with the results obtained within the local density functional method.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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