YU ISSN 0015-3206
FZKAAA 13 (1) 73 (1981)

CHARGE DENSITY DISTRIBUTIONS AROUND CHEMISORBED HYDROGEN FROM MODEL CALCULATIONS

B. GUMHALTER and V. ZLATIĆ

Institute of Physics of the University, 41001 Zagreb, Yugoslavia

Received 22 October 1980

UDC 538.971

Original scientific paper

Charge density distributions around a hydrogen atom adsorbed on a surface of a high density free electron metal ($r_s = 2.07$) have been calculated on the basis of the formerly developed model of extra-orbital screening with the use of the parameters extracted from the corresponding bulk problem of hydrogen absorption.

Recent model calculations of nonlinear screening of a proton embeded into a free electron gas$^{1)}$ have revealed a great similarity between the results obtained from two different approaches to screening of a charged impurity. The first approach based on the local density functional method (LDF) has been used by Almbladh et al.$^{2)}$ and Norskov$^{3)}$ for calculating the change of the density of states and the heat of solution due to introduction of a hydrogen atom into a free electron metal. The second approach employed by the authors$^{1)}$ used Anderson's phenomenological nonorthogonal extra-orbital Hamiltonian$^{4,5)}$ and Friedel's concept of screening for calculation of the change in the density of states and the screening charge around an impurity (proton) embeded into a free electron gas. The comparison of the results obtained by these two methods, LDF calculations and those based on the model Hamiltonian with appropriately determined parameters, shows that they are in a remarkably good agreement as regards the screening properties of the metal. This has emphasized once more the great relevance of the Anderson approach in description of such systems and consequently brought to the fore the need of the evaluation of the parameters characteristic of the model.

The approach to screening developed by the authors is based on the calculation of the total change in the density of states $\Delta N(\omega)$ upon introducing the neutral atom into a free electron gas. In the Anderson model $\Delta N(\omega)$ is given by the derivative of the extra-orbital phase shift:

$$\Delta N(\omega) = -2 \frac{\partial}{\partial \omega} \frac{1}{\pi} \operatorname{Im} \ln (\omega - \varepsilon_a - \Sigma_a(\omega)) \tag{1}$$

where ε_a is the effective energy of the hydrogen 1s orbital state $|a\rangle$ and

$$\Sigma_a(\omega) = \Lambda(\omega) - \mathrm{i}\Delta(\omega) = \sum_k |V_{ak} - \omega S_{ak}|^2 G_k^0(\omega) \tag{2}$$

is the a-orbital self-energy expressed in terms of the matrix elements V_{ak} which couple the metal electron states $|k\rangle$ to the hydrogen valence state $|a\rangle$. The overlap integral $S_{ak} = \langle a | k \rangle$ is present here due to the nonorthogonality of the basis set $\{|k\rangle, |a\rangle\}$ and G_k^0 is the Green's function of the electron states in the unperturbed metal. To evaluate V_{ak} the authors have employed the overlap approximation

$$V_{ak} = \sum_b \langle a | V | b \rangle \langle b | k \rangle \approx V_{aa} S_{ak} \tag{3}$$

which assumes that the diagonal term gives a dominant contribution in the summation over the atomic states. The integral S_{ak} depends on the structure of the metallic band and in inhomogeneous systems it is a function of the spatial position of the impurity valence orbital. As has been shown in Ref. 1, in the case of hydrogen embeded into a homogeneous free electron gas S_{ak} is an even function of k which reaches its maximum at the band bottom. This gives rise in $\Delta N(\omega)$ to a formation of a doubly occupied bound state pinned to the band bottom and the appearance of an antiresonance in the band region in order to preserve the charge neutrality of the system.

In this communication we continue to study an entirely different situation in which the atom is moved towards the metal surface, i. e. into a highly inhomogeneous region as regards the metal electron wavefunctions[6]. In this case S_{ak} becomes predominantly and odd function of k with a maximum near k_F for high metallic densities. A different overlap causes a redistribution of the spectral weight in $\Delta N(\omega)$ towards the Fermi level: disappearance of the bound states bellow the band bottom and formation of a resonance near the Fermi energy E_F. On the other hand, in contrast to the spatial dependence of the overlap integral, we do not anticipate any drastic changes in the matrix element V_{aa} when the atom is moved towards the surface since, expect for screening, V_{aa} is believed to depend mainly on the atomic structure of the impurity. Starting from these two premises we shall use some of the parameters obtained in the bulk problem to calculate the charge density structure for the case of hydrogen adsorbed on a free electron surface.

In order to get the values of V_{aa} for adsorption on a high density substrate we repeat the calculation described in Ref. 1 for $r_s = 2.07$ characteristic of Al. This gives magnitude of $V_{aa} = -0.0550$ Ry (1Ry = 13.6 eV) which indicates a strong screening of the atomic potential by the high density electron gas and the importance of the overlap effects in the determination of the values of Λ and Δ. The derivation of the expression for the local density of states $\Delta N(\vec{r}, \omega)$ in terms of V_{aa} and the matrix elements of the unperturbed Green's operator $\langle a | G^0 | r \rangle$ has been given in Ref. 6. To carry out the calculations for S_{ek}, functions Λ, Δ and $\langle a | G^0 | r \rangle$ we must specify the geometry of the system. In this letter we make the same simplest possible choice as in Ref. 6 by placing the hydrogen atom at the edge of the infinite square barrier (IBM) which simulates the surface of a semi-infinite free electron gas described by the sine wave functions in the direction perpendicular to the surface. The distance between the adatom and the positive background egde coincides then with the equilibrium distance found earlier in the LDF approach to the jellium surface problem$^{7,8)}$. The evaluation of S_{ak} is performed by expanding the substrate wave functions into spherical harmonics and retaining only the contributions of s, p and d partial waves ($l = 0, 1, 2$). In this approximation we get:

$$S_{ak} = -12 \left(\frac{\pi a_B^3}{2V} \right)^{1/2} P_1 (\cos \vartheta_k) \frac{a_B k}{(1 + (a_B k)^2)^2}, \tag{4}$$

where a_B is the Bohr radius and ϑ_k is the angle between the vector $\vec{k}$ and the positive z direction. This expression clearly illustrates the effect of different spatial boundary conditions on the symmetry of S_{ak} with respect to the bulk case (c. f. Ref. 1). Different overlap also gives rise to different Λ and Δ when compared with the corresponding expressions for a homogeneous system:

$$\Delta (\omega) = 6 (V_{aa} - \omega)^2 \frac{\omega^{3/2}}{(1 + \omega)^2} \Theta (\omega) \tag{5}$$

and

$$\Lambda (\omega) = 6 (V_{aa} - \omega)^2 \left\{ \left[\frac{1}{16 (1 + \omega)} + \frac{3}{8 (1 + \omega)^2} + \frac{1}{(1 + \omega)^4} - \frac{3}{2 (1 + \omega)^3} \right] \Theta (\omega) - \frac{3 (|\omega| + 4 \sqrt{|\omega|} + 1)}{8 (1 + |\omega|)^4} \Theta (-\omega) \right\} \tag{6}$$

where both V_{aa} and ω are dimensionless quantities measured in Rydberg units.

The behaviour of Δ and $\Delta (\omega)$ near the band bottom (which follows the surface electronic density of states $\sim \omega^{3/2}$) supresses the values of its Hilbert transform $\Delta (\omega)$ in this interval and hence gives rise to only one intersection of the line $\omega - \varepsilon_a$ with Λ in the band below E_F. Since the maximum in $\Delta N (\omega)$ is approximately determined by this intersection the structure of the change in the density of states will be characteristic of a simple resonance plotted in Fig 2. The shape and the position of this resonance are in a remarkably good agreement with results of the LDF calculations of Lang and Williams$^{7)}$ for $r_s = 2$.

In Fig. 3 we have shown the spatial variation of various components of the adatom induced screening charge density $\Delta N (\vec{r})$ in the direction perpendicular to the surface and inward the metal. The component derived from the atomic orbital exhibits the expected exponential attenuation with the distance from the proton

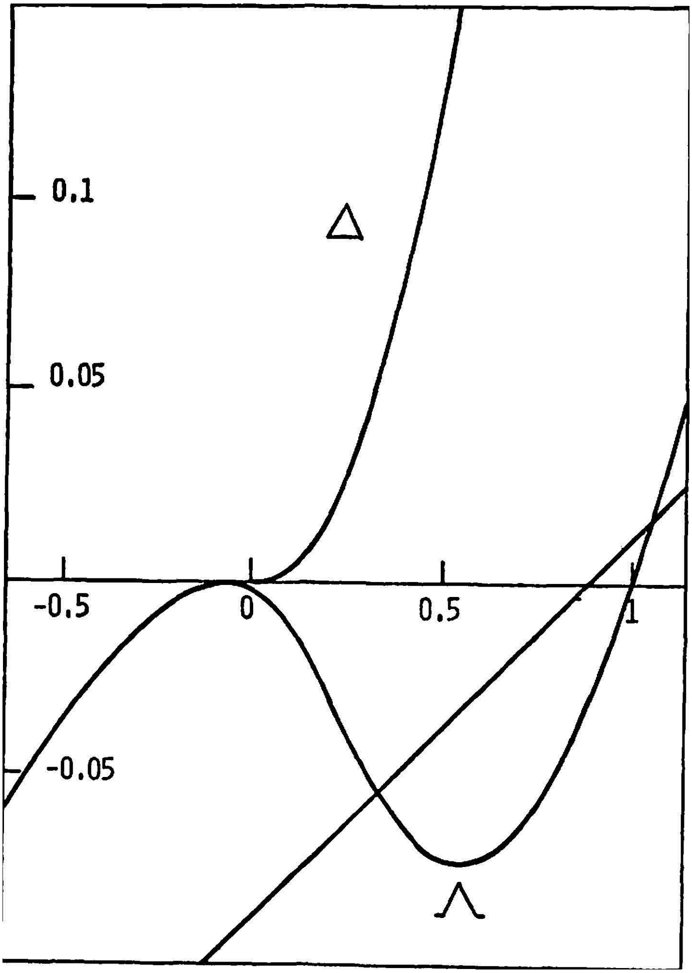

Fig. 1: Functions Λ and Δ for H atom located at the edge of IBM for $V_{aa} = -0.550$. The line $\omega - \varepsilon_a$ with $\varepsilon_a = 0.8940$ Ryd is also shown (1Ry = 13.6 eV).

whereas the component derived from the substrate states (extra-orbital charge) reaches a maximum at the unperturbed orbital radius, then falls off exponentially and starts oscillating at $r = 2.5\ a_B$. At larger distances it approaches the limit of Friedel's oscillations with the period π/k_F. For distances exceeding $4a_B$ the orbital derived component becomes negligible and the total sreening density is composed of only the substrate derived, extra-orbital charge. The spatial features of the total screening charge density may be considered as representative of neutral chemisorption in which there is no appreciable charge transfer from the adsorbate to the substrate or vice versa. The electronic occupation of the orbital derived states which amounts to $N_a = 0.9167$ may be regarded as a confirmation of intra-orbital nature of screening in this system.

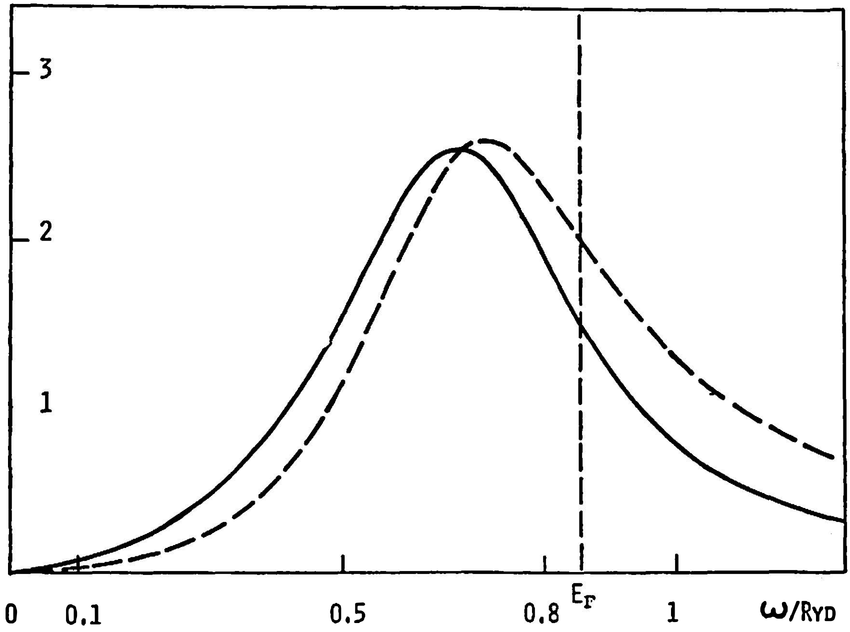

Fig. 2: Full curve: total change in the density of states: dashed curve: change in the state density derived from the orbital states whose occupation is $N_a = 0.9167$. $E_F = 0.85517$ Ryd (1 Ry = 13.6 eV).

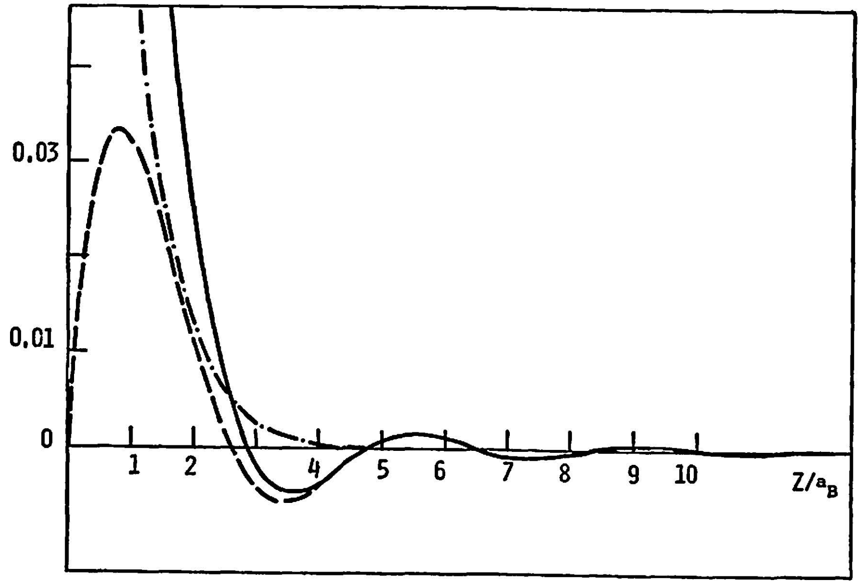

Fig. 3: Total screening charge density (full curve), extra-orbital component (dashed curve) and intra-orbital component (dash-dotted curve) for the inward direction perpendicular to the surface.

The present model enables also the calculation of $\Delta N(\vec{r})$ in various directions. However, due to the crudeness of the approximation in which the surface was replaced by IBM the results become spurious for directions nearly paralel to the surface. For this reason we haven't attempted to give the contour plots of the charge density which have been studied by other authors within the LDF calculations[7,9].

Acknowledgment

The first author would like to acknowledge useful discussions with N. D. Lang. Thanks are also due to V. Lepčin for technical assistance.

References

1) B. Gumhalter and V. Zlatić, J. Phys. C **13** (1980) 1679;

2) C. O. Almbladh, U. von Barth, Z. D. Popović and M. J. Stott, Phys. Rev. B **14** (1976) 2250;

3) J. K. Norskov, Phys. Rev. B **20** (1979) 446;

4) P. W. Anderson, Phys. Rev. **124** (1961) 41;

5) P. W. Anderson and W. L. McMillan, Proc. Int. School »Enrico Fermi«, Varenna 1966 (Academic Press, 1967, ed. W. Marshall);

6) B. Gumhalter and V. Zlatić, J. Phys. C **12** (1969)L 339;

7) N. D. Lang and A. R. Williams, Phys. Rev. Lett. **34**(1975) 531;

7) N. D. Lang and A. R. Williams, Phys. Rev. Lett. **34**(1975) 531 ibid, **37** (1976) 212;

8) O. Gunnarsson, H. Hjelmberg and B. I. Lundqvist, Phys. Rev. Lett. **37**(1976)292;

9) H. Hjelmberg, Physica Scripta **18**(1978)481.

RASPODJELA GUSTOĆE NABOJA OKO KEMISORBIRANOG VODIKA DOBIVENA IZ MODELNOG RAČUNA

B. GUMHALTER i V. ZLATIĆ

Institut za fiziku Sveučilišta, 41001 Zagreb

UDK 538.971

Originalni znanstveni rad

Izračunata je raspodjela gustoće naboja oko atoma vodika adsorbiranog na površini slobodno-elektronskog metala visoke gustoće ($r_s = 2.07$) na osnovi već prije razvijenog modela, a pomoću parametara nađenih u odgovarajućem modelu vodikove absorpcije.