

## Electron structure of interstitial hydrogen in $\alpha$ -Zr

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**Abstract.** The impurity-induced charge density in jellium is calculated by solving the Schrödinger equation self-consistently. The resulting phase shifts have been used to estimate the value of residual resistivity for dilute Zr-H system, which comes out to be  $0.50 \mu\Omega \text{ cm/at.}\%$ . An alternative form of one-parameter-screened Coulomb potential, which is more suitable than the customary Thomas-Fermi potential, is suggested. The calculated self-energy by using new potential is found close to its value obtained by Darby *et al.*

**Keywords.** Electron structure; interstitial hydrogen; induced charge density; host-impurity potential; self-energy; residual resistivity.

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### 1. Introduction

Considering the linear screening approximation for the proton-electron interaction, we have calculated the activation energy for interstitial H in  $\alpha$ -Zr (Singh *et al* 1981). The energy was found to be minimum at octahedral(O)-sites as the ionic density is minimum around this position due to site symmetry. Darby *et al* (1978) treated the screening of the proton in hcp  $\alpha$ -Zr semiempirically. Their calculated relative energies of hydrogen at tetrahedral(T)- and O-interstitial-sites of the hcp lattice show that proton prefers to occupy the T-interstitial-site in  $\alpha$ -Zr, which is in accordance with the diffraction experiments (Narang *et al* 1977). They also represent the potential due to impurity by the screened Coulomb potential  $V_{sc}(r) = e \exp(-\gamma r)/r$  where the parameter  $\gamma$  is determined by the Friedel sum rule. The perturbed charge density  $\Delta n(r)$  is obtained from  $V_{sc}(r)$  by solving Poisson's equation. An unsatisfactory feature of this potential is that the charge density derived from it diverges at the origin, while the true charge density must be finite everywhere. The minimum energy value of hydrogen at T-position indicates that electron proton electrostatic interaction contributes significantly to the energy. It is now well established that electron proton interaction is very strong and this interaction cannot be substituted by a weak potential with the same

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scattering properties. As a consequence, theoretical information is limited to a few solids. Although atomic hydrogen is a simplest solute in a metal that can be thought of, a comprehensive theory of metal-hydrogen interactions has yet to be developed. The screening of a proton in jellium density corresponding to Cu was first carried out by Friedel (1952) by solving a set of one-particle Schrödinger equations self-consistently. In recent past, an attempt to include the exchange and correlation effects in this approach has been made by Popovic *et al* (1976) and Almbladh *et al* (1976) in the study of nonlinear screening of a proton in the jellium density corresponding to Al and Mg. Since then a number of groups have published similar results (Zaremba *et al* 1977; Manninen *et al* 1977; Jena and Singwi 1978). For a proton in a simple metal, reliable numerical results for the heat of solution have been obtained recently within various refinements of jellium model (Manninen and Nieminen 1979; Perrot and Rasolt 1981; Craig 1983). Efforts have also been made to study the electronic structure of hydrogen in noble and transitional metals (Jena *et al* 1977; Sholl and Smith 1978; Smith 1978; Perrot and Rasolt 1982).

The energy calculations of a proton involve host-impurity potential, in turn, this depends upon the electron-proton interaction. Therefore, it is necessary to incorporate the proton screening due to Fermi gas with utmost care, for which a self-consistent calculation is required. In this paper, we have calculated the induced charge distribution around an impurity, the host-impurity potential by solving Schrödinger equation using density functional formalism due to Hohenberg and Kohn (1964) and Kohn and Sham (1965). The resulting phase shifts at Fermi surface are used to estimate the residual resistivity of dilute metal-hydrogen system. One of the aims of this paper is also to propose an alternative potential which yields a charge density and which is finite at the origin and gives good quantitative results when applied to a simple problem of a metal.

The plan of the paper is as follows: The necessary formalism is presented in §2. The calculations and results are presented in §3 with our conclusions in §4.

## 2. Nonlinear screening and screened Coulomb potential

The Hamiltonian for the metal plus single hydrogen impurity may be written as (Sholl and Smith 1978):

$$H_{MH} = -\frac{1}{2}\nabla^2 + U(\mathbf{r}) + eV(\mathbf{r}) + V_{xc}(n(\mathbf{r})), \quad (1)$$

where  $eV(\mathbf{r})$  is the additional Coulomb potential energy due to the impurity.  $U(\mathbf{r})$  is the interaction potential due to metallic ions.  $V_{xc}(n(\mathbf{r}))$  is the functional derivative of a universal exchange and correlation energy functional of the electron mean density. The total charge density  $n(\mathbf{r})$  for the complete system now is written as

$$n(\mathbf{r}) = n_0(\mathbf{r}) + \Delta n(\mathbf{r}). \quad (2)$$

$V(\mathbf{r})$  and  $\Delta n(\mathbf{r})$  are related by Poisson's equation

$$\nabla^2 V(\mathbf{r}) = -4\pi\Delta n(\mathbf{r}). \quad (3)$$

Ideally the potential  $V(\mathbf{r})$  and the charge density  $\Delta n(\mathbf{r})$  should be determined self-consistently so that the eigenstates of the Hamiltonian (1) produce a charge density which is identical to that obtained from equation (3). In the crystal the conduction band

states are represented by the Bloch functions. As a result the impurity site will no longer be having the spherical symmetry of jellium model and the direct solution of second order partial differential equation for a single electron eigen states is no longer possible. The success has been achieved recently in the self-consistent solution for a proton in jellium by taking a part of  $U(\mathbf{r})$  which is spherically symmetric around impurity (Manninen and Nieminen 1979; Perrot and Rasolt 1981, 1982). Very recently, the Green's function matrix method has been extended to include the bandstructure description of the host metal (Craig 1983).

In order to find improved potential one can consider the case of electron gas which is simple and related problem. This corresponds to  $U(\mathbf{r}) = 0$  in (1). This system has been studied extensively by Popovic *et al* (1976). Following Popovic *et al*, induced electronic charge density is written as

$$\begin{aligned} \Delta n(\mathbf{r}) &= n(\mathbf{r}) - n_0(\mathbf{r}) \\ &= \frac{1}{\pi^2} \int_0^{k_f} dk k^2 \sum_{l=0}^{\infty} (2l+1) [\{R_{lk}(r)\}^2 - j_l^2(kr)] + 2[R_b(r)]^2, \end{aligned} \quad (4)$$

where  $\mathbf{k}$  is the electron wave vector and  $k_f$  is the Fermi momentum. The sum over angular momentum quantum number  $l$  in (4) converges very rapidly. This is because the effective potential is localized so that the radial wave functions  $R_{lk}(r)$  for large  $l$  will differ little from the unperturbed electron Bessel functions  $j_l(kr)$ . S-type bound state sometimes occur; therefore, the bound state charge density is also added in (4). In the present calculations the bound state with two electrons is considered.

Single electron eigen values  $\varepsilon_k$  and corresponding radial function  $R_{lk}(r)$  are obtained by solving the following one particle radial equation:

$$\left[ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(r) + \frac{l(l+1)}{2r^2} - \varepsilon_k \right] r R_{lk}(r) = 0. \quad (5)$$

For the continuum states  $\varepsilon_k = k^2/2$ , zero of energy is taken to be the potential far from the impurity where its effect is almost vanished. Thus the effective potential field, in which the electron moves, is

$$V_{\text{eff}}(r) = -\frac{Z}{r} + \int \frac{\Delta n(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{xc}}(n(r)) - V_{\text{xc}}(n_0(r)), \quad (6)$$

where  $Z$  is the effective charge of the impurity ion. The parametrized form of  $V_{\text{xc}}(n(r))$  proposed by Hedin and Lundqvist (1971) has been adopted for the detailed calculation. For a spherically symmetric potential field, (5) and (6) are solved self-consistently following the procedure of Popovic *et al* (1976). To start with the host-impurity screened Coulomb potential

$$V_{\text{ir}}(r) = -\frac{Z}{r} \exp(-\alpha r^\beta), \quad (7)$$

is taken for  $V_{\text{eff}}(r)$ . With parameter  $\beta$  fixed, the parameter  $\alpha$  was determined so that the Friedel sum rule

$$Z = \frac{2}{\pi} \sum_l (2l+1) \delta_l(k_f), \quad (8)$$

is satisfied with high accuracy. The radial equation is solved numerically in the steps of 0.05 a.u. out to a radius  $R_0 = 10$  a.u. The resulting radial wave functions are used to generate  $\Delta n(r)$ , which in turn, generate  $V_{\text{eff}}(r)$ . By varying  $\beta$  this iterative procedure is repeated until both the trial potential  $V_{\text{tr}}(r)$  and self-consistent potential  $V_{\text{eff}}(r)$  satisfy the Friedel sum rule simultaneously. The first seven phase shifts  $\delta_l(k_f)$  have been used to satisfy (8) as their values become too small for  $l > 6$ . The induced electron density,  $\Delta n(r)$ , is calculated by using the first seven partial radial waves obtained by varying  $\mathbf{k}$  from  $0 \rightarrow k_f$ . A 40-point Gauss quadrature formula is used to integrate over  $\mathbf{k}$ . The bound state wave function  $R_b(r)$  and energy  $\varepsilon_b$  are determined by matching the numerical solution to the asymptotic solution given by equation

$$rR_b(r) \sim \exp[-k_0 r], \quad (9)$$

where  $k_0 = (-2\varepsilon_b)^{1/2}$ , at  $r = R_0$ , the distance at which the potential is set equal to zero, where it becomes negligibly small.

An alternative simple one-parameter-screened Coulomb potential function, which has been shown to provide an accurate description of a proton impurity in both electron gas and a transitional metal (Sholl and Smith 1978), is

$$V_{\text{sc}}(r) = -Z \left( 1 + \frac{\gamma r}{2} \right) \exp(-\gamma r)/r. \quad (10)$$

The parameter  $\gamma$  was chosen to satisfy the Friedel sum rule.  $V_{\text{sc}}(r)$  via Poisson's equation yields a simple analytical form of induced charge density:

$$\Delta n(r) = \frac{z\gamma^3}{8\pi} \exp(-\gamma r). \quad (11)$$

Obviously this  $\Delta n(r)$  is finite at the origin. Physical quantities, such as Knight shift, which depend upon the screening charge near the nucleus would certainly be described more accurately for new potential. The simple functions  $V_{\text{sc}}(r)$  and  $\Delta n(r)$  given in (10) and (11), respectively, lead on to evaluate the self-energy of the induced charge analytically. As a result the self-energy, which is defined as

$$E_{\text{self}} = \frac{1}{2} \int V_{\text{sc}}(r) \Delta n(r) dr, \quad (12)$$

reduces to

$$E_{\text{self}} = -\frac{3Z^2\gamma}{32} \text{ a.u.} \quad (13)$$

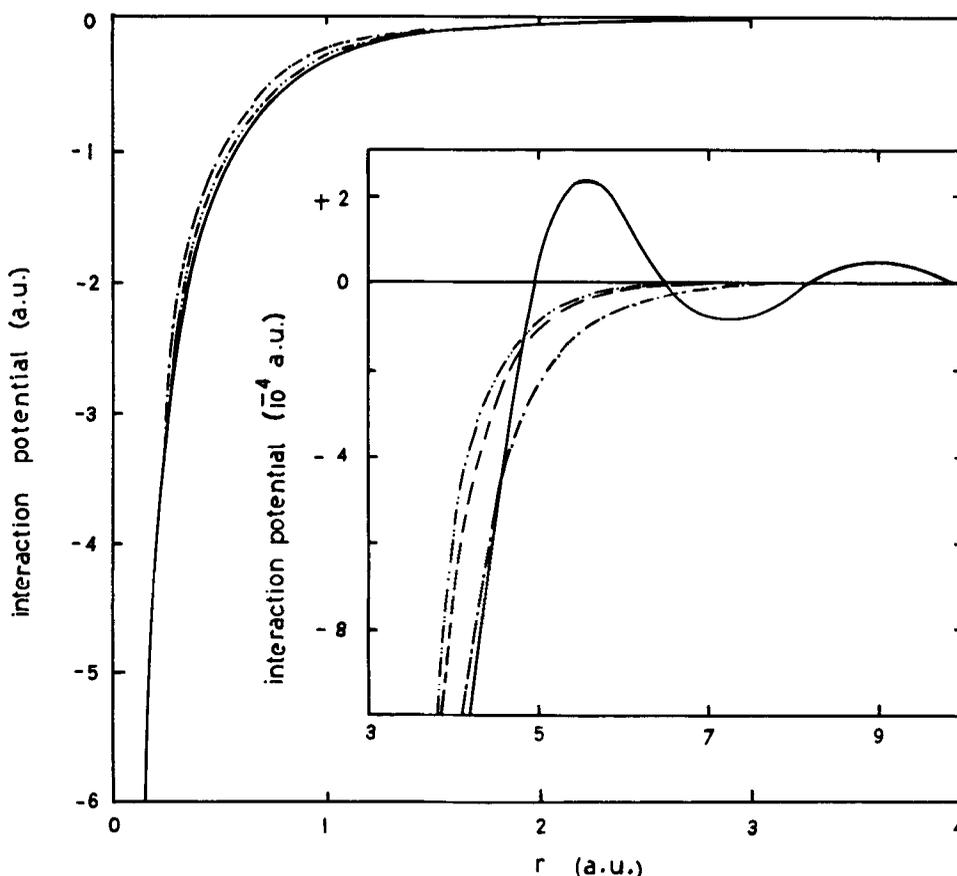
However, for charge density appropriate to the Thomas-Fermi potential this energy is  $-Z^2\gamma/4$  a.u. It is to be noted that the value of  $E_{\text{self}}$  ( $= -5Z^2\gamma/32$ ) reported by Sholl and Smith (1978) is in error.

### 3. Calculations and results

The calculations have been performed for dilute hydrogen impurity in jellium density appropriate to  $\alpha$ -Zr ( $r_s = 2.1076$  a.u.). Effective charge  $Z = 1$  is considered on the impurity ion.

### 3.1 Host-impurity potential

The self-consistent effective potential given by (6) is shown in figure 1. The magnitude of the potential decreases rapidly and becomes negligible beyond Wigner-Seitz radius. In the inset, the potential is plotted on magnified scale beyond  $r = 3$  a.u. to show the Friedel oscillations clearly. The calculated screened potential  $V_{tr}(r)$  is also shown in figure 1 for comparison. The parameters  $\alpha$  and  $\beta$  of trial potential are found to be 1.1445 a.u. and 1.1740 a.u., respectively. The two potentials are almost equal upto  $r = 2.5$  a.u. They can be separated from each other, if we plot them on magnified scale. At larger distances,  $V_{tr}(r)$  decreases exponentially while  $V_{eff}(r)$  exhibits Friedel oscillations, which are of small magnitude. We have determined the parameter of the screened potential  $V_{sc}(r)$  by fitting it to the self-consistent potential, which satisfies the Friedel sum rule. This potential is shown by dash-double-dot line in figure 1. Apart from the absence of small Friedel oscillations in  $V_{sc}(r)$  the agreement with  $V_{eff}(r)$  for  $\gamma = 1.9$  a.u. is excellent. The interactions upto the second nearest neighbour dominate in the binding of an impurity (Prakash *et al* 1979); the analytical expression for the

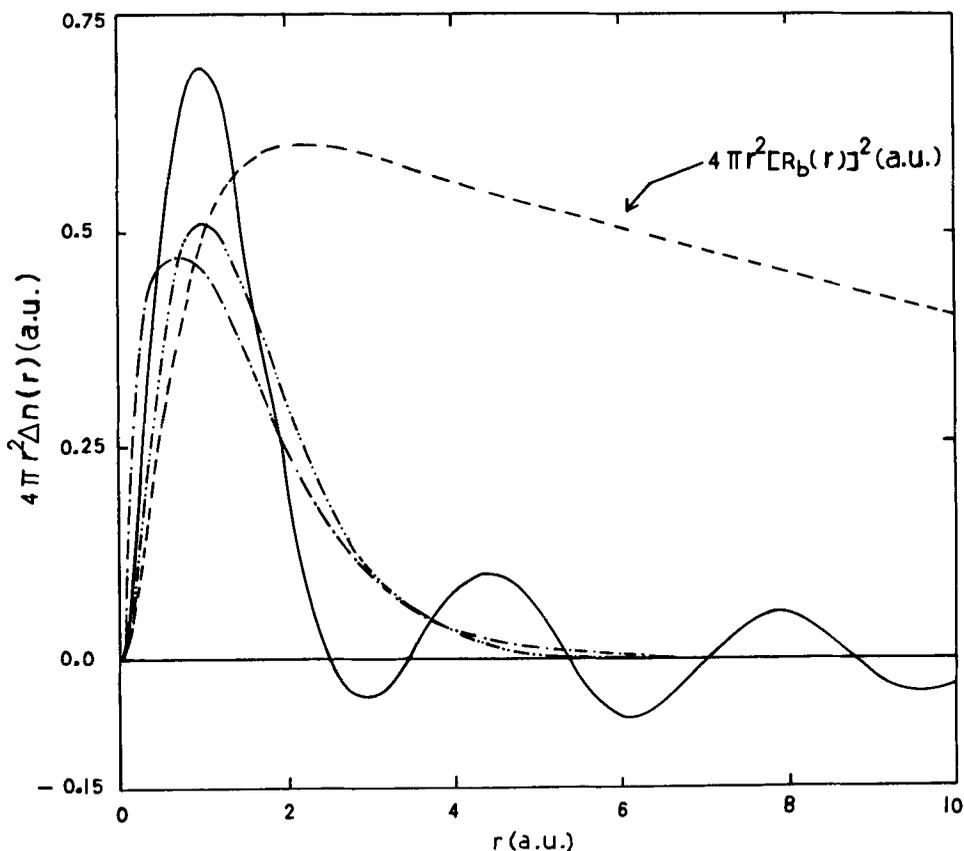


**Figure 1.** The self-consistent potential  $V_{eff}(r)$  (solid line), trial potential  $V_{tr}(r)$  (dashed line) and screened potential  $V_{sc}(r)$  (dash-double dot line) for hydrogen in jellium density corresponding to  $\alpha$ -Zr ( $r_s = 2.1076$  a.u.).  $V_{sc}(r)$  (dash-dot line) is due to Darby *et al* (1978) corresponding to screening parameter 1.35 a.u.

potential given in (10) should, therefore, be more satisfactory in the theory of *H* in metals than the Thomas-Fermi screened Coulomb potential taken by Darby *et al* (1978). Their one-parameter screened potential is also shown in figure 1 for comparison.

### 3.2 Electronic charge distribution

The change in electronic charge distribution around an impurity  $\Delta n(r)$  is calculated using (4). The spherically symmetric induced charge distribution around impurity  $4\pi r^2 \Delta n(r)$  is shown in figure 2 as a function of  $r$ . It is quite evident that there is a big pile-up of charge near the impurity. As we move further away from the impurity, the charge density decreases rapidly. Beyond 2.5 a.u. distance it becomes oscillatory. The induced charge density derived from (11) is also shown in figure 2 by dash-double-dot line. This,  $4\pi r^2 \Delta n(r)$ , describes all the gross features of the self-consistent charge density except the Friedel oscillations which are of small magnitude. Their contribution to the self-



**Figure 2.** Induced density  $4\pi r^2 \Delta n(r)$  (solid line) and unnormalized weakly bound electron density  $4\pi r^2 [R_b(r)]^2$  (dashed line) for hydrogen in jellium density corresponding to  $\alpha$ -Zr ( $r_s = 2.1076$  a.u.).  $4\pi r^2 \Delta n(r)$  (dash-double dot line) is derived from (11) for  $\gamma = 1.9$  a.u. Induced density (dash-dot line) is due to Darby *et al* (1978) corresponding to screening parameter 1.35 a.u.

energy of the charge density should therefore be small. Since this self-energy is the most significant contribution to the energy of  $H$  in metals which depends upon  $\Delta n(r)$ , an approximate charge density which describes all the gross features of  $\Delta n(r)$  but not the Friedel oscillations should be satisfactory. Our calculated self-energy from (13) for  $\gamma = 1.9$  a.u.,  $-0.356$  Ryd, is very close to the value of it,  $-0.375$  Ryd, found by Darby *et al* (1978). The induced charge density  $4\pi r^2 \Delta n(r)$  appropriate to Thomas-Fermi potential (Darby *et al* 1978) is also shown in figure 2 for comparison.

An S-type shallow bound state of energy  $-0.00036$  a.u. is also found in our calculations. To show the weak binding of s-electrons in  $H$  atom, the unnormalized charge density  $4\pi r^2 [R_b(r)]^2$  of bound electrons is shown in figure 2. It is quite evident that the contribution of two bound electrons in this state to  $\Delta n(r)$ , within the sphere of radius 10 a.u., is only about 0.02. It indicates that the bound state in question is extended extensively in real space. To include the total bound state contribution in  $\Delta n(r)$ , one has to extend the calculations approximately upto  $R_0 = 100$  a.u. However, it has been seen that the parameters  $\alpha$  and  $\beta$ , and the correlation energy were changed by less than  $\frac{1}{2}\%$  by doubling  $R_0$ ; halving the integration interval or using 64—rather than 40—point Gauss integration formula. This whole procedure is repeated with the adjusted values of  $\alpha$  and  $\beta$  until the correct Friedel sum is obtained. A small change in the values of potential parameters by doubling  $R_0$  is observed because the proton field is highly localized. In the jellium density corresponding to Al ( $r_s = 2.064$  a.u.), earlier workers found somewhat different values of bound state; Jena and Singwi (1978) and Popovic *et al* (1976) determined  $\epsilon_b$  to be  $-0.000175$  a.u. and  $-0.0005$  a.u., respectively. While Zaremba *et al* (1977) derived the value to be  $-0.00013$  a.u. for the jellium density  $r_s = 2$  a.u. These differences in calculated values for the bound state energy arise from small variations in the total perturbing potential which is very sensitive to the screening component of  $\Delta n(r)$ . Jena and Singwi, for example, found that their value for  $\epsilon_b$  changed significantly with the inclusion of the gradient correction term for the exchange and correlation potential, while only small changes in  $\Delta n(r)$  are observed. Another reason to obtain different values for  $\epsilon_b$  is the different accuracies involved in calculating  $\Delta n(r)$ . For example, Zaremba *et al* (1977) have used only 24—instead of 40—point Gauss quadrature formula to evaluate the integral over  $\mathbf{k}$ . It has been found that if we use 10—point Gauss integration formula and decrease the mesh size by half, the bound state vanishes altogether, while the perturbing potential shows hardly any significant deviation.

### 3.3 Residual resistivity

The residual resistivity,  $\Delta\rho$ , is estimated using the following expression (Blatt 1957):

$$\Delta\rho = \frac{2.732}{k_f Z_H} \sum_{l=0}^{\infty} (l+1) \sin^2(\delta_l - \delta_{l+1}), \quad (14)$$

where  $k_f$  is in atomic units and  $Z_H = 4$  for Zr matrix.  $\Delta\rho$  for dilute Zr-H system is calculated using the first seven phase shifts as the values of  $\delta_l$  become too small for  $l > 6$ . Our calculated value of  $\Delta\rho$  is  $0.50 \mu\Omega \text{ cm/at.}\%$ . However, the experimental value of residual resistivity for Zr H<sub>1.54</sub> is available in the literature (Bickel and Berlincourt 1970). The derived value of  $\Delta\rho$  for this zirconium hydride composition comes out to be  $0.27 \mu\Omega \text{ cm/at.}\%$ . The resistivity of Zr (high purity) at 4.2 °K is  $0.213 \mu\Omega \text{ cm}$ .

#### 4. Conclusion

A simplified but realistic physical model is adopted to study the nonlinear screening around an impurity in  $\alpha$ -Zr. It has been found that the new screened Coulomb potential function given in this paper provides a good description of an impurity in transitional metal host. The analytical expression of  $\Delta n(r)$  given by (11) will be preferred over its analytical form obtained from Thomas-Fermi potential for calculating the electronic properties of an impurity, because the former describes all the gross features of the self-consistent-induced charge density. The electronic structure  $\Delta n(r)$  near the impurity site is found to be very sensitive to small changes in the overall potential. Therefore, it is expected that a more rigorous treatment incorporating both the band structure of the host metal and the non-spherical features of the interstitial site would yield additional important structure in  $\Delta n(r)$ .

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