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Characterization of the electronic density of metals in terms of the bulk modulus

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In the present work a semiempirical method for characterizing the electronic density of pure metals (or, equivalently, the mean radius, r_s, per electron) from the bulk modulus is proposed. The general features of this method are discussed and shown to be simple and useful for many situations. Knowledge of r_s is important because it determines several important properties of the metal. For instance, the interaction with a hydrogen impurity is dominated by the interstitial electron density, and we check the applicability of the obtained values of r_s by evaluating the volume of solution of hydrogen in pure metals. Our results are in excellent agreement with the available experimental data.

1. Introduction

The electronic density $n(\mathbf{r})$ of a metallic system is a fundamental quantity for the microscopic interpretation of many of its properties as well as of several relationships between them. However, a general scheme for obtaining $n(\mathbf{r})$ is quite difficult to implement. Thus, it is customary to approximate it by, for instance, a superposition of (corrected) atomic densities or linearized Thomas–Fermi screening clouds, or even by an effective homogeneous electron gas density. Among these approximations, the uniform electron gas is widely used because of its simplicity. This is particularly useful when dealing with low-symmetry perturbations, and, in principle, this model should work well if the property of interest depends mainly on the free mobile part of the electron density.

Different criteria for assigning an r_s value ($\frac{4}{3}\pi r_s^3 = 1/n_0$) for each metal have been proposed in the literature. Usually they are related to the valence of the atoms or to the corresponding plasma frequency [1]. However, several properties of metals, such as the bulk modulus or the response of the metal to a point perturbation, cannot be well represented by these criteria. Other definitions for the r_s values that can account for these properties in an appropriate way have been reported in the literature [1–3], but these definitions are rather difficult to apply. In this paper, we propose to obtain the effective electronic density (or, equivalently, the effective parameter r_s) from the experimental bulk modulus B of the metal. Our method is shown to be very simple and to give very good results, therefore being generally preferable to previous methods.

In Section 2 we describe the method that we propose to relate r_s to B. We evaluate r_s for pure metals and make a comparison with other values given in the literature [1–3]. As an example, in Section 3 we apply the obtained r_s values to the calculation of the volume of solution of hydrogen in metals v_H and compare these results with the available experimental data.

2. Procedure for assigning r_s effective values to metallic systems

One of the first steps in the systematic analysis of the properties of metals throughout the periodic table is to characterize them by means of their electronic density. The jellium model represents the simplest approximation, where the metal is described in terms of a uniform homogeneous electron gas of density $n_0 = 3/4\pi r_s^3$ (atomic units are used throughout). Thus, r_s defines the radius of the sphere corresponding to one electron in the jellium. The applicability of this model to real metals seems reasonable when we are interested in properties that depend on the free-electron-like component of the density. This is the case for the elastic properties of metals, which depend essentially on the interstitial electronic density. The main contribution to this density comes from the s and p electrons in simple metals, with an additional contribution due to the d valence electrons in the case of the transition metals [4].

The bulk modulus, B, is an example of an easily measurable elastic property which depends mainly on the compression of the electronic density at the interstitial positions. Hence [4]

$$B = \frac{1}{12\pi r_s}\left(\frac{\partial^2 \varepsilon}{\partial r_s^2} - \frac{2}{r_s}\frac{\partial \varepsilon}{\partial r_s}\right)$$

The energy, ε, per particle can be written as the sum of the kinetic ($\varepsilon_{\text{kin}} = 3/5\alpha^2 r_s^2$), exchange ($\varepsilon_x = -3/2\pi\alpha r_s$)

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and correlation ($\varepsilon_c = \varepsilon(r_s)$) energies (where $\alpha = (4/9\pi)^{1/3}$). The correlation energy ε_c is always negative, and its value depends on the range of the parameter r_s. At metallic densities, it goes from $0.1\varepsilon_x$ to $0.5\varepsilon_x$. In the limit of high densities, it is proportional to $\ln r_s$. Replacing in the expression for B, we obtain

$$B = B_{\mathrm{kin}} + B_x + B_c$$

with

$$B_{\mathrm{kin}} = \frac{1}{2\pi}\frac{1}{\alpha^2 r_s^5}, \quad B_x = -\frac{1}{2\pi^2}\frac{1}{\alpha r_s^4}, \quad B_c = B_c(r_s)$$

In Fig. 1, we plot the bulk modulii of pure metals against r_s for the interstitial density, given by different workers [1–3]. We note that there is a clear correlation in these data, which is reasonably well reproduced on the average by the bulk modulus of the jellium, except at low densities (large values of r_s) which is the case for the alkali metals. Improving the fitting, the corrected semiempirical parametrization

$$B(r_s) = \begin{cases} B_{\mathrm{kin}} + (B_x + B_c) & \text{if } r_s \leqslant 1 \\ B_{\mathrm{kin}} + \dfrac{1}{r_s}(B_x + B_c) & \text{if } r_s > 1 \end{cases} \qquad (1)$$

is in excellent agreement with the experimental data, now including the alkali metals.

This new parametrization of B given in Equation 1 provides us with a semiempirical definition of r_s in terms of the bulk modulus B. This parameter is much simpler than the other definitions proposed in the literature [1, 2, 3, 5].

In conjunction with Equation 1, we used the experimental values of B reported in the literature [6, 7] as an input for obtaining the parameter r_s for pure metals (Table I).

In Fig. 2 we show our values of r_s through the periodic table compared with the values given by other workers. The overall trend is coincident with those r_s obtained from other criteria [1–3]. No systematic differences among the different models is observed. For instance, Nørskov [3], who calculated r_s in a more complicated way, by averaging the interstitial density sampled by the electrostatic potential of a dissolved hydrogen atom, however, obtained values very close to ours.

3. Application of the r_s values to the calculation of v_H

Our semiempirical parametrization of B versus r_s given in Equation 1 provides a simple alternative definition of r_s. This can be useful for a great variety of situations in which the electronic density is perturbed in the interstitial region of the metal. In particular, this is the case for a hydrogen atom interstitially dissolved in a metal host. This impurity produces an expansion of the metal lattice represented by the volume, v_H, of solution. The calculation of this quantity is quite complicated and very difficult to perform in a systematic way through the periodic table.

Using the theory of the effective medium, Nørskov and Lang [8] and Stott and Zaremba [5] obtained a parametrization of the energy of an atom embedded in a inhomogeneous system. The idea is to

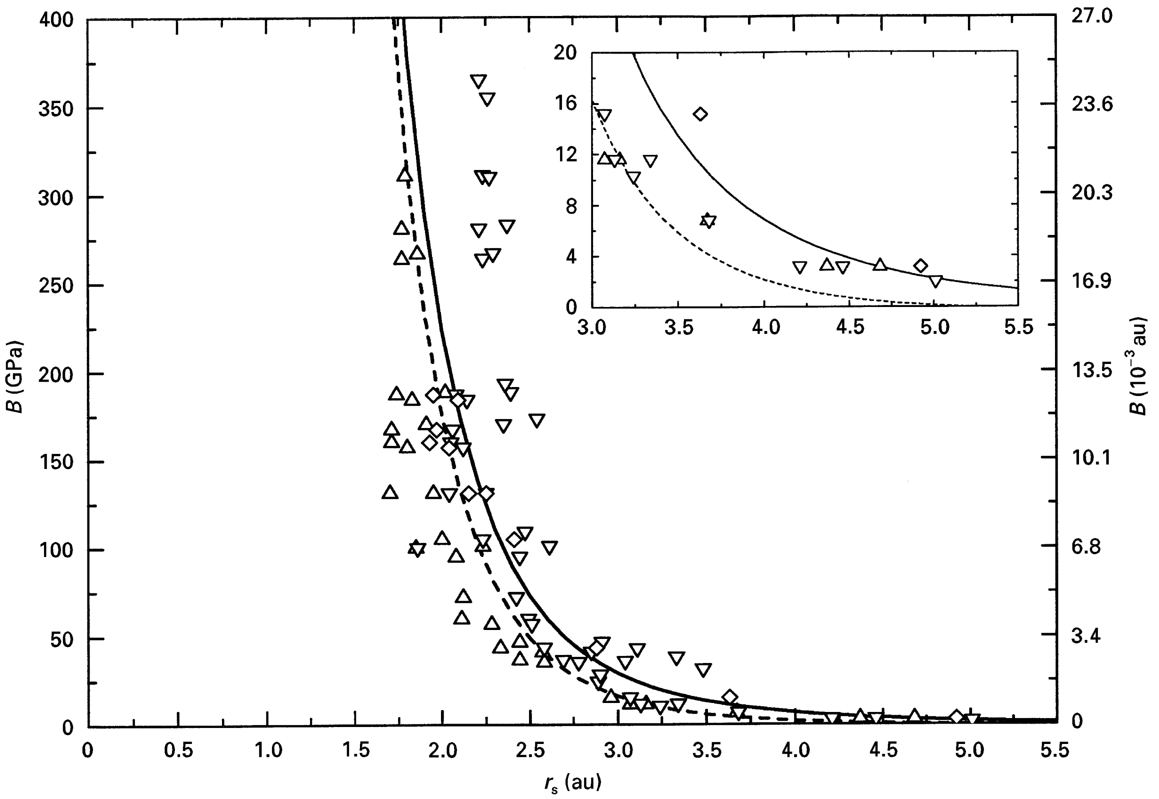

Figure 1 Bulk modulus versus r_s (– – –), $B = B_{\mathrm{kin}} + B_x + B_c$ for pure metals; (—), our parametrization of B, Equation (1); (△), experimental values from Moruzzi *et al.* [1]; (▽), experimental values from Perrot and Rasolt [2]; (◇), experimental values from Nørskov [3].

TABLE I Bulk moduli B and parameters r_s for pure metals, where the experimental values for B are taken from [6, 7] and r_s is calculated from Equation 1

Element	Li	Be											B	C
B (GPa)	11.6	100											178	
r_s (au)	3.61	2.35											2.09	
Element	Na	Mg											Al	Si
B (GPa)	6.81	35.4											72.1	
r_s (au)	4.01	2.89											2.51	
Element	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
B (GPa)	3.18	15.2	43.5	105	157	160	131	167	187	184	131	59.8	56.8	
r_s (au)	4.67	3.42	2.77	2.33	2.15	2.14	2.23	2.12	2.08	2.08	2.23	2.60	2.63	
Element	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
B (GPa)	3.14	11.6	36.6	95	170	264	281	311	267	188	101	46.7	41.1	
r_s (au)	4.68	3.61	2.87	2.37	2.11	1.94	1.91	1.88	1.93	2.07	2.35	2.74	2.80	
Element	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb
B (GPa)	2.03	10.3	24.3	109	193	310	365	410	355	283	173	28.2	35.9	42.9
r_s (au)	5.10	3.69	3.11	2.31	2.06	1.88	1.82	1.78	1.83	1.91	2.11	3.02	2.88	2.78
Element	Fr	Ra	Ac											
B (GPa)	1.96	13.2	24.5											
r_s (au)	5.14	3.52	3.11											

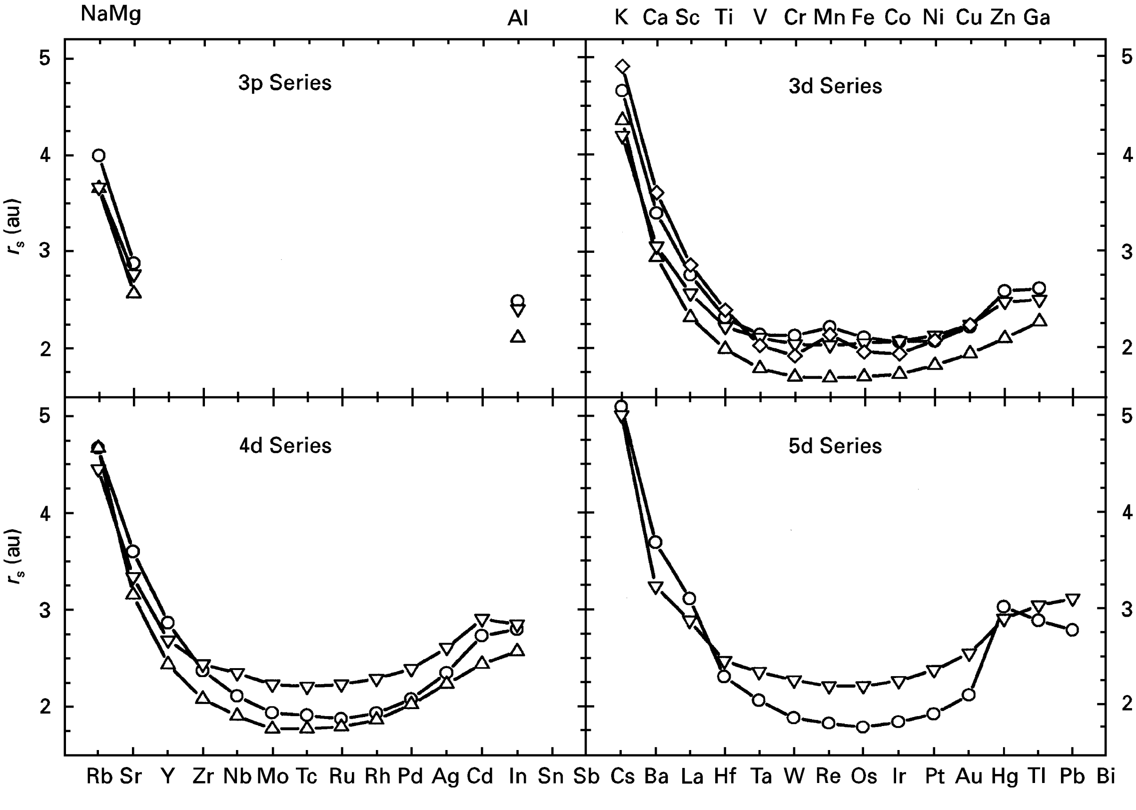

Figure 2 Values of r_s for pure metals. (○) this work; (△), from Moruzzi *et al.* [1]; (▽), from Perrot and Rasolt [2]; (◇), from Nørskov [3].

approximate this system by jellium with effective density, n_0. Theoretically, the volume, v_H, of solution is given by the slope of this energy with respect to n_0.

The change, δE, of energy associated with an isotropic and homogeneous deformation introduced by one hydrogen in the metal determines the volume of solution through the expression [9]

$$v_H = \frac{V_H}{\Omega} = \frac{1}{\Omega}\frac{\delta\Omega}{\delta P}\sum_i \frac{\delta \boldsymbol{R}_i}{\delta\Omega}\cdot\frac{\delta E}{\delta \boldsymbol{R}_i} = -\frac{1}{B}\sum_i \frac{1}{3}\frac{\boldsymbol{R}_i}{\Omega}\cdot\frac{\delta E}{\delta \boldsymbol{R}_i}$$

where Ω is the volume per atom of the metal, B is the bulk modulus and $\delta \boldsymbol{R}_i$ is the deformation at the positions, $\{\boldsymbol{R}_i\}$, of the ions of the metal. To first order in $\{\delta \boldsymbol{R}_i\}$, and using the Hellmann-Feynmann theorem [10, 11], δE is given by the electrostatic interaction between the ionic cores of the metal and the impurity of charge Z_0 at $\boldsymbol{r} = \boldsymbol{0}$.

$$\delta E = \sum_i Z_i \left(\int \frac{\Delta n(\boldsymbol{r}) - Z_0 \delta(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{R}_i|^3} (\boldsymbol{R}_i - \boldsymbol{r})\, \mathrm{d}^3\boldsymbol{r} \right) \cdot \delta \boldsymbol{R}_i$$

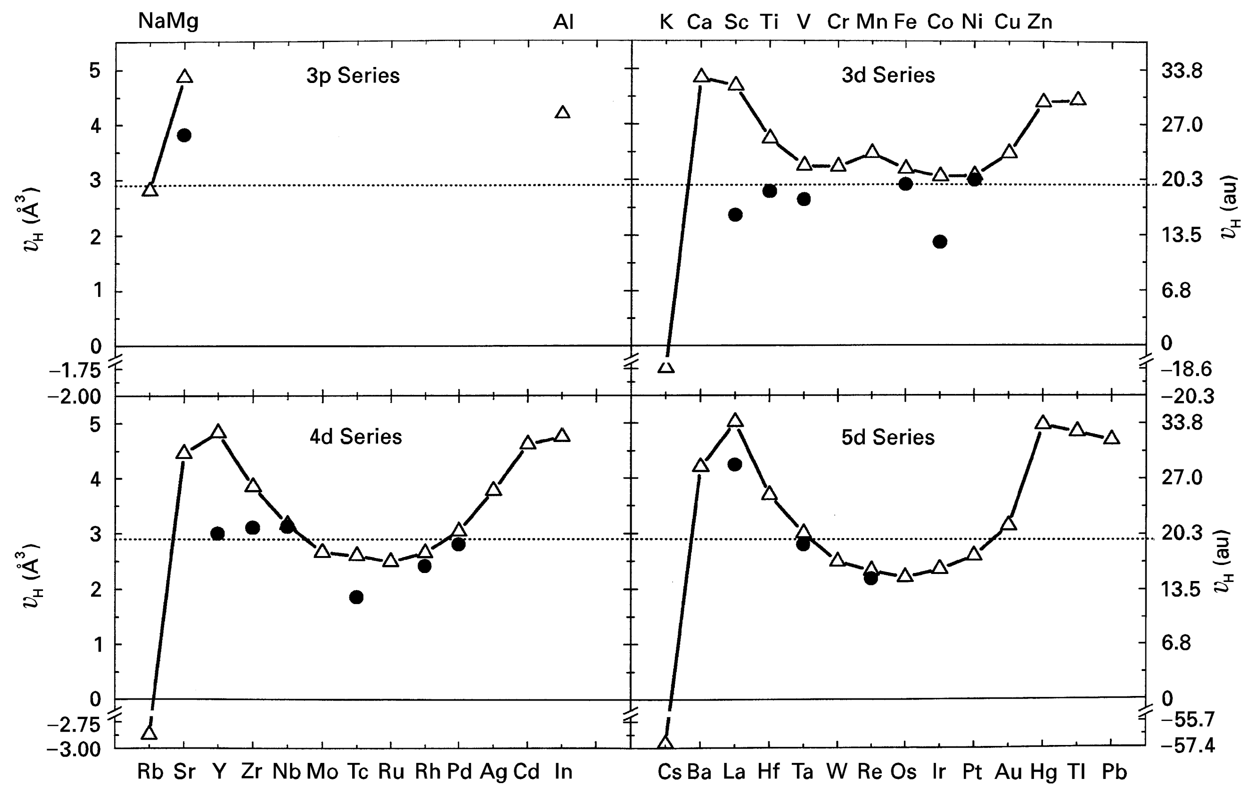

Figure 3 Values of v_H for pure metals. (△), this work; (●), experimental values [12–19].

Here Z_i is the charge of the ion located at $\boldsymbol{R}_i$ and $\Delta n(\boldsymbol{r})$ is the charge density induced by the impurity, which depends on the effective parameter r_s.

In Fig. 3, we compare v_H calculated using the values of r_s obtained from Equation 1, with the available experimental data [12–19]. We observe that our results reproduce the overall tendencies of v_H through the periodic table and are in good quantitative agreement with the scarce existing experimental data.

Several workers have emphasized that hydrogen produces an approximately constant relaxation $v_H = 2.9$ Å^3 in a great variety of metals and alloys [12–14]. So far there has been no satisfactory explanation for this fact. As shown in Fig. 3, our calculation shows that this rule is valid only for transition metals owing to the similarity of their interstitial densities and the smooth dependence of v_H on r_s in that region (see Fig. 2). This rule does not necessarily need to be valid for other metals or alloys.

4. Summary

We presented a new method for assessing the r_s parameters for metals. This method not only provides a new listing of significant r_s values for pure metals but also is simple enough to apply easily to almost any metallic system. As an example, we apply the obtained r_s values to the calculation of the volume, v_H, of solution of hydrogen in metals, a quantity that is rather difficult to measure but very important because it determines several properties of the metal–hydrogen interaction. The agreement with existing experimental data is considered excellent.

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