Investigación *Revista Mexicana de Física* **33** *No. 1(1987) 23–33*

Calculation of the Knight Shift of metallic hidrogen and its volume dependence

M.A. Solís and L.F. Magaña

Instituto de Física, Universidad Nacional Autónoma de México,
Apdo. Postal 20-364, 01000 México, D.F.

(recibido el 7 de mayo de 1986; aceptado el 6 de octubre de 1986)

Abstract. We have made a calculation of the Knight Shift of metallic hydrogen using the formalism of Hohenberg, Kohn and Sham. With this formalism we calculated self consistently the electronic density in the metal. For the electron spin susceptibility we have used two expressions. One given by Shastry and the other given by Von Barth and Hedin. We have considered the proton in an interstitial position and in a substitutional position. The maximum obtained value for the Knight Shift is 8.28×10^{-5} (which corresponds to an interstitial position) and the minimum value we obtained is 7.97×10^{-5} (which corresponds to a substitutional position) at atmospheric pressure. We have performed the calculation of the Knight Shift for six different volume changes, with a maximum decrease in volume of 18%, for each one of the proton positions.

Resumen. Hemos calculado el cambio Knight para hidrógeno metálico usando el formalismo de Hohenberg, Kohn y Sham. Con este formalismo calculamos autoconsistentemente la densidad elctrónica en el metal. Para la susceptibilidad de espín electrónica hemos usado dos expresiones, una dada por Shastry y la otra por Von Barth y Hedin. Hemos considerado al protón en una posición intersticial y en una sustitucional. El valor máximo que obtuvimos para el cambio Knight es 8.28×10^{-5} (el cual corresponde a la posición intersticial), el valor mínimo es 7.97×10^{-5} (que corresponde a la posición sustitucional), ambas a presión atmosférica. Los cálculos de cambio Knight los realizamos para seis cambios de volumen, con una disminución máxima en el volumen de 18%, para cada uno de los tipos posiciones del protón.

PACS: 76.60-k; 76.60 cq

1. Introduction

Recently, there has been considerable interest on metallic hydrogen [1–11]. The prediction and knowledge of its properties is becoming important. In this work we are interested on the prediction of the Knight Shift for this material.

The fractional shift, K, produced by the hyperfine Hamiltonian [12] in the nuclear magnetic resonance frequency in a metal, with respect to the resonance frequency for the same nucleus in a non metallic environment is known as the Knight Shift. If we have the metal nucleus with magnetic moment $\boldsymbol{\mu}$ at the origin of coordinates, the interaction of this nucleus with an effective magnetic field produced by the surrounding electrons is usually described by the hyperfine Hamiltonian [12]:

$$\begin{aligned} H_h = {} & \frac{8\pi}{3}\,\boldsymbol{\mu}\cdot\mathbf{m}(0) \\ & - 2\mu_B\boldsymbol{\mu}\cdot\int\left\{\frac{\mathbf{m}(\mathbf{r})}{r^3}-\frac{3\mathbf{r}[\mathbf{r}\cdot\mathbf{m}(r)]}{r^5}\right\}d\mathbf{r} + 2\mu_B\sum_j \boldsymbol{\mu}\cdot\frac{\mathbf{L}_j}{r_j^3}\,, \end{aligned} \tag{1}$$

with

$$\mathbf{m}(\mathbf{r}) = 2\mu_B\sum_j \mathbf{S}_j\delta(\mathbf{r}-\mathbf{r}_j),$$

where $\mathbf{S}_j$ and $\mathbf{L}_j$ are the operators of spin and angular momentum in units of $\hbar$ for the electron at position $\mathbf{r}_j$.

Following Refs. 6–9 we take for metallic hydrogen an FCC structure, with a value of the electronic density parameter $r_s = 1.0$ (in atomic units and $(4/3)\pi r_s^3 = (1/n_0)$, where n_0 is the average electron density in the metal). Bearing this in mind we examine the contributions to Eq. (1).

The first term in Eq. (1) is by far the largest term in this Hamiltonian in most simple metals. It is the usual Fermi contact interaction and comes from all electrons in the crystal with a wave function different from zero at the site of the nucleus. The second term describes the magnetic interaction between the nuclear and electron spin dipoles. If the origin is located at a site with cubic symmetry (as in our case) this term vanishes identically. The last term is the magnetic coupling between the nuclear spin and the electron orbital magnetic moments. This term is expected to be important mainly in transition metals with half filled *d*-bands, although there is some evidence that can be important for other simpler metals like Berillium [13, 14]. This term is usually negligible for simple metals and it is extremely difficult to calculate accurately in metals. In our case, for metallic hydrogen, we will not take it into account.

For a uniform external magnetic field B in the z-direction, the Fermi contact contribution to the Knight Shift is given by

$$K_s = \frac{8\pi}{3}\frac{m(0)}{B}, \tag{2}$$

where $m(0)$ is the value at the site of the nucleus of the component of the total electron magnetic moment density along the direction of the external magnetic fiel B. This expression can be compared with the original expression for the Knight Shift given by Townes *et al* [15], which is

$$K_d = \frac{8\pi}{3}\chi_p \Omega_c P_F, \tag{3}$$

where χ_p is the electron spin susceptibility per unit volume, Ω_c is the volume of the unit cell and P_F is the average over the Fermi Surface of the square of the valence electron wave functions evaluated at the nucleus. Equation (2) takes into account core and valence electrons with wave functions different from zero at the site of the nucleus, below the Fermi Surface and on the Fermi Surface. The contribution to $m(0)$ in Eq. (2) can be written as [13]

$$m(0) = m_{FS}(0) + m_{FV}(0), \tag{4}$$

where $m_{FS}(0)$ corresponds to the valence electrons on the non-perturbed Fermi Surface, and $m_{FV}(0)$ comes from electrons in the volume enclosed by this Fermi Surface.

The contribution $m_{FV}(0)$ can be divided in the following way [13]:

$$m_{FV}(0) = m_{\text{val}}(0) + m_c(0), \tag{5}$$

where $m_{\text{val}}(0)$ corresponds to the valence electrons (enclosed in the Fermi Surface) contribution and $m_c(0)$ comes from the core electrons.

The contribution to the Knight Shift from the electrons on the Fermi Surface, K_{FS}, presents a very small difference [13] ($< 0.6\%$) with respect to the value of the Knight Shift obtained using Eq. (3).

For metallic hydrogen we don't have core electrons, so the contribution to the Knight Shift from the core electrons is zero, the contribution to the Knight Shift, K_{val}, from the valence electrons inside the Fermi Surface is usually neglected (see Refs. from 16 to 20). This contribution seems to be between 0.6% and 5% of the value of K_{FS} (or K_d). Thus, we will neglect the contribution K_{val} for the case of metallic hydrogen, following the usual approach, and the only contribution to the Knight Shift to be considered for the case of metallic hydrogen is K_{FS} which is, as we have said, practically identical to K_d [13].

In section 2 we present a summary of the Formalism of Hohenberg, Kohn and Sham [22, 23] which we have used to calculate K_d. We have done the calculation considering two approaches. In the first we consider the proton in an interstitial position [16]. In the second we consider the proton in a substitutional position [17].

Section 3 is used to present results and discussion.

2. Electronic densities from non-linear screening

The central result of the Hohenberg-Kohn-Sham formalism [22, 23] states that there exists a one body local potential $V_{\text{eff}}(\mathbf{r})$ which through the one body Schrödinger equation given by

$$\left[-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \tag{6}$$

generates the set of wave functions $\psi_i(\mathbf{r})$ and the exact ground state density of the system trough the independent particle density expression:

$$n(\mathbf{r}) = \sum_{\epsilon_i<\epsilon_f} |\psi_i(\mathbf{r})|^2, \tag{7}$$

where the sum extends up to the Fermi energy.

The effective potential is given by

$$V_{\text{eff}}(\mathbf{r}) = -\phi(\mathbf{r}) + \frac{\delta E_{xc}[n(r)]}{\delta n(\mathbf{r})}, \tag{8}$$

where $\phi(\mathbf{r})$ is the total electrostatic potential of the system, and $E_{xc}[n(\mathbf{r})]$ is the exchange-correlation energy of the system.

When we omit gradient corrections, we can write

$$\frac{E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{d}{dn}\Big[n(\mathbf{r})\epsilon_{xc}(n(\mathbf{r}))\Big], \tag{9}$$

where $\epsilon_{xc}(n(\mathbf{r}))$ is the exchange-correlation per particle in a homogeneous electron gas of density n.

Using spherical symmetry, we write down the equation to be solved for our case:

$$\left[-\tfrac{1}{2}\,\frac{d^2}{dr^2} + V_{\text{eff}}(r) + \frac{\ell(\ell+1)}{r^2}\,\epsilon_k\right] r R_{\ell k}(r) = 0, \tag{10}$$

where $R_{\ell k}(r)$ is a solution to the radial Schrödinger equation of energy $\epsilon_k = k^2/2$.

Notice that the potential of the impurity in the electron gas is contained in $\phi(\mathbf{r})$ and that in the absence of the impurity, $R_{\ell k}(r)$ is proportional to the spherical Bessel function of the first kind, $J_\ell(kr)$.

From Eq. (7) we can obtain the electron displaced density around an ion in the electron gas:

$$\Delta n(\mathbf{r}) = \sum_{\epsilon_i < \epsilon_f} |\psi_i(\mathbf{r})|^2 - n_0 \tag{11}$$

or

$$\begin{aligned}\Delta n(\mathbf{r}) = \frac{1}{\pi^2}\sum_{\ell=0}^{\infty}(2\ell+1)\int_0^{k_F} dk\, k^2\left[|R_{\ell k}(r)|^2 - |J_\ell(kr)|^2\right]\\ + 2\sum_b |\psi_b(r)|^2,\end{aligned} \tag{12}$$

where $\psi_b(r)$ refers to the bound state wave functions.

For the exchange-correlation contribution to the effective potential, Eq. (9), we use the expression given by Hedin and Lundqvist [24], in atomic units:

$$V_{xc}(\mathbf{r}) \equiv \frac{E_{xc}[n(r)]}{\delta n(r)} = -0.02909\left[\frac{21}{r_s} + 0.7734\ln\left(1+\frac{21}{r_s}\right)\right], \tag{13}$$

where $(4/3)\pi r_s 3 = 1/n_0$.

The electrostatic potential obeys Poisson's equation:

$$\nabla^2\phi = -4\pi D(r), \tag{14}$$

where

$$D(\mathbf{r}) = Z\delta(\mathbf{r}) + n_0 - n(\mathbf{r}) \tag{15}$$

and Z is the charge of the nucleus, or

$$D(\mathbf{r}) = Z\delta(\mathbf{r}) - \delta n(\mathbf{r}). \tag{16}$$

In order to have $V_{\text{eff}}(\mathbf{r})$ vanishing at large r, the exchange correlation part is rescaled to

$$V_{xc}(\mathbf{r}) \rightarrow V_{xc}[n(\mathbf{r})] - V_{xc}[n_0]. \tag{17}$$

Notice that Eqs. (14) and (15) correspond to an ion within the gas. If we consider that the ion is located at the center of a vacancy in the Jellium, the corresponding electrostatic potential, ϕ, is generated by a density given by [25]

$$D(r) = Z\delta(r) + n_0\,\Theta(r - r_s) - \delta n(r), \tag{18}$$

where $\Theta(x)$ is the step function.

We solved self consistently Eqs. (10), (12), (13), (16) and (17). We carried out the calculation of the density following the method of Manninen *et al.* [26] to achieve automatic self consistency.

For the case of the ion at the center of a vacancy in the jellium, the set of equations to be solved is (10), (12), (13), (17) and (18).

For the solution to the equations of the Formalism of Hohenberg, Kohn and Sham we can obtain P_F which is the value of the square of the wave function of conduction electrons, at the origin, averaged over the Fermi Surface.

In the next section we give the results for the Knight Shift for metallic hydrogen considering a proton in an interstitial position and a proton in a substitutional position. For the first case, the charge neutrality of the metal is preserved by introducing one electron in the gas after introducing the proton [6, 8]. The change in the density is negligible (we have added one electron in a system with 10^{23} electrons). For the second case the charge neutrality is preserved by removing a sphere of positive charge equal to the charge of a proton, as indicated in Eq. (18) and then introducing the proton [25].

3. Results and Discussion

We have used Eq. (3) to calculate the Knight Shift for metallic hydrogen. For the electron spin susceptibility we have used the one given by Shastry [27] and the one given by Von Barth and Hedin [28]. In table I we show the normalized Knight Shift for metallic hydrogen as a function of volume using the expression given by Shastry [27] for the magnetic susceptibility. In this table we show results for a proton in an interstitial position. Table II shows the results for the normalized Knight Shift considering a proton in a vacancy and using the expression for the magnetic susceptibility given by Shastry [27]. In table III and IV we report the same variables but using the expression given by Von Barth and Hedin [28] for the magnetic susceptibility. The values for the Knight Shift of metallic hydrogen are about four times smaller than the value for lithium which is the smallest value reported previously. This is not surprising because it is known that the Knight Shift is a decreasing function of the atomic number [16].

At atmospheric pressure the largest value we found for the Knight Shift corresponds to an interstitial position of the proton and using the expression of Shastry [27] for the magnetic suscep-

V/V_0, %	$K_d(V)/K_d(0)$	χ_p (10^{-6} cgs vol. units)
0	1.0000	3.000
3	0.9985	3.026
6	0.9979	3.052
9	0.9970	3.079
12	0.9960	3.107
15	0.9952	3.135
18	0.9945	3.164

TABLE I. Volume dependence of the normalized Knight Shift for metallic hydrogen (interstitial position) using the magnetic susceptibility given by Shastry [27].

V/V_0, %	$K_d(V)/K_d(0)$	χ_p (10^{-6} cgs vol. units)
0	1.0000	3.000
3	1.0009	3.026
6	1.0018	3.052
9	1.0026	3.079
12	1.0035	3.107
15	1.0044	3.135
18	1.0053	3.164

TABLE II. Volume dependence of the normalized Knight Shift for metallic hydrogen (substitutional position) using the magnetic susceptibility given by Shastry [27].

tibility, and is 8.28×10^{-3}%. The smallest value we found for the Knight of metallic hydrogen at atmospheric pressure corresponds to a proton in jellium vacancy and using the expression given by Von Barth and Hedin [28] for the magnetic susceptibility and this value is 7.97×10^{-3}%.

The variation of the Knight Shift for metallic hydrogen with volume is shown in Fig. 1. It is practically a linear behavior for the cases we studied. However, for the case of the interstitial position, the

V/V_0, %	$K_d(V)/K_d(0)$	χ_P (10^{-6} cgs vol. units)
0	1.0000	2.979
3	0.9984	3.005
6	0.9977	3.031
9	0.9966	3.058
12	0.9956	3.085
15	0.9947	3.113
18	0.9939	3.141

TABLE III. Volume dependence of the normalized Knight Shift for metallic hydrogen (interstitial position) using the magnetic susceptibility given by Von Barth and Hedin [28].

V/V_0, %	$K_d(V)/K_d(0)$	χ_P (10^{-6} cgs vol. units)
0	1.0000	2.979
3	1.0008	3.005
6	1.0016	3.031
9	1.0024	3.058
12	1.0032	3.085
15	1.0040	3.113
18	1.0048	3.141

TABLE IV. Volume dependence of the normalized Knight Shift for metallic hydrogen (substitutional position) using the magnetic susceptibility given by Von Barth and Hedin [28].

Knight Shift increases when the volume decreases and this happens using any of the two expressions for the magnetic susceptibility we have considered. For the case of the substitutional position of the proton we have an increasing Knight Shift when the volume decreases, for any of the two magnetic susceptibilities we used.

At present there is a tendency to believe that the properties of simple metals are better predicted using an ion in a vacancy in jellium [25, 29] (*i.e.* in a substitutional position), so that we believe that the correct volume dependence of the Knight Shift for metallic hydrogen is to increase when the volume decreases, as shown in Fig. 1.

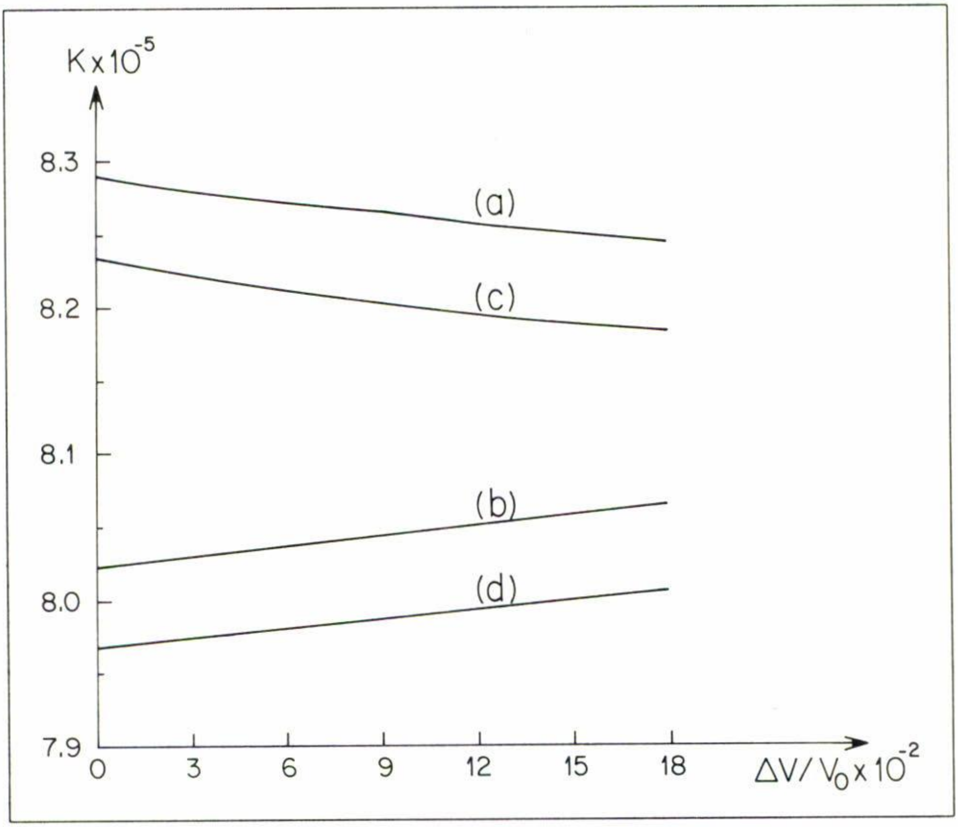

FIGURE 1. Volume dependence of the Knight Shift for metallic hydrogen. *a)* Interstitial position and using Shastry's magnetic susceptibility [27]; *b)* Substitutional position and using Shastry's magnetic susceptibility [27]; *c)* Interstitial position and using Von Barth and Heding result for the magnetic susceptibility [28]; *d)* Substitutional position and using the result of Von Barth and Hedin for the magnetic susceptibility [28].

References

1. N.W. Ashcroft, *Phys. Rev. Lett.* **21** (1968) 1748.
2. T. Schneider, and E. Stoll, *Physica* **55** (1969) 702.
3. T. Schneider, *Helv. Phys. Acta* **42** (1969) 957.
4. E.G. Brovman, Yu Kagan, and A. Kholás, *Soviet Phys. JETP* **34** (1972) 1300.
5. L.G. Caron, *Phys. Rev. B* **12** (1974) 5024.
6. M.D. Whitmore, J.P. Carbotte, and R.C. Shukla, *Can J. Phys.* **57** (1979) 1185.
7. L.F. Magaña, *Phys. Lett.* **80***A* (1980) 193.
8. L.F. Magaña, M.D. Whitmore, J.P. Carbotte, *Can J. Phys.* **60** (1982) 424.
9. L.F. Magaña, M.A. Ocampo, *Phys. Rev. B*, in press, 15 May (1986).
10. A.H. McDonald, C.P. Burgess, *Phys. Rev. B* **26** (1982) 2849.
11. C.E. Campbell, J.G. Zabolitzky, *Phys. Rev. B* **29** (1984) 123.
12. G.C. Carter, L.H. Bennet, D.J. Kahan, *Prog. Mater. Sci.* **20** (1977) 153.
13. L. Wilk, M. Nusair, S.H. Vosko, *Can J. Phys.* **59** (1980) 585.
14. R.E. Walstedt, Y. Yafet, *Solid State Commun.* **15** (1974) 1855.
15. C.H. Towner, C.Herring, W.D. Knight, *Phys. Rev.* **77** (1950) 852.
16. E. Zaremba, D. Zobin, *Phys. Rev. Lett.* **44** (1980) 175.
17. M. Manninen, P. Jena, *J. Phys. F* **10** (1980) 1567.
18. G.A. Styles, G. Transfield, *J. Phys. F* **8** (1978) 2035.
19. Setsuro Asano, Jiro Yamashita, *J. Phys. Soc. Jap.* **34** (1973) 1223.
20. B.Y. Tong, M.M. Pant, *Phys. Rev. B* **6** (1972) 1195.
21. L.Wilk, S.H. Vosko, *Can J. Phys.* **59** (1981) 888.
22. W. Kohn and L.J. Sham, *Phys. Rev. A* **140** (1965) 1133.
23. P. Hohenberg, W. Kohn, *Phys. Rev. B* **136** (1964) 864.
24. L. Hedin, B.I. Lundqvist, *J. Phys. C* **4** (1971) 2064.
25. M. Manninen, P. Jena, R.M. Nieminen, J.K. Lee, *Phys. Rev. B* **24** (1981) 7057.
26. M. Manninen, R. Nieminen, P. Hautojarvi, J. Arponen, *Phys. Rev. B* **12** (1975) 4012.
27. B.S. Shastry, *Phys. Rev. B* **17** (1978) 385.
28. U. Von Barth, and L. Hedin, *J. Phys. C* **5** (1972) 1629.
29. M. Manninen, P. Jena, *J. Phys. F* **10** (1980) 1567.