Knight Shifts in Simple Metals: A Single-Ion Approach

E. Zaremba and D. Zobin
Department of Physics, Queen's University, Kingston K7L 3N6, Canada

(Received 27 August 1979)

We present a linear-response formulation of Knight shifts in metals based on the density-functional theory. The approach emphasizes the importance of achieving self-consistency with respect to both the charge and spin densities and includes core polarization. An application to simple metals indicates that, in this case, the Knight shift is essentially a local property, independent of structure. Satisfactory agreement with experiment is achieved.

Knight-shift measurements in metals and alloys are of interest because they provide a delicate probe of both the electronic and magnetic properties in the vicinity of the resonant nucleus. In spite of the extensive theoretical work done in this field,[1-3] it can still be said that a description of the Knight shift which consistently incorporates all effects that have been considered important (such as self-consistency and core polarization) is still lacking. It is the purpose of this Letter to propose a new method of dealing with the problem from a fundamental point of view with use of the density-functional theory.[4,5] To illustrate the method we have performed Knight-shift calculations for several of the simple metals. The main conclusion of our approach is that the Knight shift for these metals can be accounted for without invoking the structural properties of the metal, but with use of a model of an ion immersed in an electron gas.

The dominant contribution to the shift is usually due to the Fermi contact interaction between the nucleus and the electronic spins and is given by[6]

$$K_s = \frac{8\pi}{3}\frac{m(0)}{B_0}. \tag{1}$$

Here, B_0 is the externally applied magnetic field and $m(0)$ is the electron-spin magnetic-moment density at the position of the nucleus. In conventional treatments of this quantity,[6] it is tacitly assumed that electronic exchange interactions give rise to a spatially *homogeneous* effective magnetic field acting on the electronic spins. This implies that the field does not alter the spatial character of the electronic band states but simply redistributes the occupation of these states at the Fermi level. With this assumption, the Knight shift is expressible as

$$K_s = \frac{8\pi}{3}\chi_s\langle|\psi(0)|^2\rangle_{E_F}, \tag{2}$$

in terms of the exchange-enhanced spin susceptibility χ_s and a Fermi-surface average of the electron contact density. Most theoretical calculations[2,3] are based on Eq. (2) with χ_s obtained either experimentally or from an independent theoretical estimate.

Although this approach has developed to an advanced level with, for example, the use of nonlocal pseudopotentials,[3] it does not consider several important effects. One of these is the exchange core polarization[1] which can be viewed as a consequence of a spatially inhomogeneous exchange field in the core of the ion. In the case of alkali metals, this effect has been estimated[7] to be of the order of 20%, although the effect appears to have a different character within the density-functional theory. Secondly, in a pseudopotential approach, the core states are taken from a free-atom calculation and thus neglect the importance of achieving self-consistency between the core and valence states in a metallic environment. Finally, in the context of the Knight shift, there is the additional requirement of achieving self-consistency between the spin density and the exchange field, a condition which is usually ignored.

To avoid these various shortcomings, it is necessary to revert to Eq. (1) and directly calculate $m(0)$. For a metal, $m(0)$ can in principle be obtained from a spin-polarized band-structure calculation with use of density-functional theory.[8] However, this direct approach is obviously difficult and, in fact, is unnecessary in those situations in which band-structure effects are of secondary importance. In this Letter we adopt an alternative method which readily accounts for the nonstructural aspects of the Knight shift in simple metals; our point of view is similar to that taken in recent calculations of muon Knight shifts.[9,10] A detailed description of the method and its applications will be the subject of a separate publication.

Our approach is a linear-response calculation done within the framework of the density-functional formalism. As shown previously,[5] the magnetization induced by an external field B_0 is given quite generally by

$$m(\vec{r}) = \int d^3r'\chi(\vec{r},\vec{r}')B_{\rm eff}(\vec{r}'), \qquad (3)$$

where $\chi(\vec{r},\vec{r}')$ is the density response function for the inhomogeneous electronic system and $B_{\rm eff}(\vec{r})$ is the effective magnetic field acting on the spins,

$$B_{\rm eff}(\vec{r}) = B_0 + \int d^3r'\, w_{\rm xc}(\vec{r},\vec{r}')m(\vec{r}'). \qquad (4)$$

In addition to the external field, Eq. (4) contains the exchange-correlation field which is defined in terms of the exchange-correlation energy functional, $w_{\rm xc}(\vec{r},\vec{r}') = \{\delta^2E_{\rm xc}[n,m]/\delta m(\vec{r})\delta m(\vec{r}')\}_{m=0}$. Our work is based on the local density approximation in which $w_{\rm xc}(\vec{r},\vec{r}')$ is of the form $w_{\rm xc}[n(\vec{r})] \times \delta(\vec{r}-\vec{r}')$.[11,12] On combining Eqs. (3) and (4) one obtains an integral equation for $m(\vec{r})$ which automatically builds in the self-consistency requirement.

It is apparent from (3) that the central quantity in our approach is the response function $\chi(\vec{r},\vec{r}')$. For computational purposes it is convenient to express χ in terms of retarded single-particle Green's functions[13]:

$$\chi(\vec{r},\vec{r}') = -2\,{\rm Im}\int_{-\infty}^{E_{\rm F}} \frac{d\omega}{\pi} G^+(\vec{r},\vec{r}',\omega)G^+(\vec{r}',\vec{r},\omega), \qquad (5)$$

where $E_{\rm F}$ is the Fermi energy. The complexity of the problem resides in the evaluation of G^+. However, a simplification suggests itself in the case of simple metals when considering the magnetic response within the Wigner-Seitz cell of a particular ion. By developing the metal Green's function in a t-matrix series,[14]

$$G^+ = G_0^+ + G_0^+t_0G_0^+ + \sum_{l\neq 0} G_0^+t_lG_0^+ + \dots,$$

only the first two terms are important for weak scattering from the surrounding ions when the spatial arguments $\vec{r}$ and $\vec{r}'$ are restricted to the Wigner-Seitz cell of interest. If the metal Green's function is approximated by the *single-ion* Green's function, $G_{\rm ion}^+ = G_0^+ + G_0^+t_0G_0^+$, we are effectively describing the propagation of an electron in the presence of a single ion imbedded in an electron gas having a density n_0 corresponding to the valence electrons. This approximation defines (and, of course, restricts) our model. To be consistent with this picture, we imagine placing a host ion at the center of a vacancy created in jellium by removing the positive background within the Wigner-Seitz radius $R_{\rm WS} = (Z_v)^{1/3}r_s$. Here Z_v is the valence charge of the ion and r_s is the electron-gas parameter, $r_s = (3/4\pi n_0)^{1/3}$. As a preliminary step in the calculation we have therefore obtained self-consistent ionic potentials using the procedure of Manninen *et al.*[15] Both core and valence states are treated on an equal footing in this calculation.

By use of the spherical-harmonic expansion, $G_{\rm ion}^+(\vec{r},\vec{r}',\omega) = \sum_L G_l^+(r,r',\omega)Y_L(\hat{r})Y_L^*(\hat{r}')$, in Eq. (5), the response to a spherically symmetric magnetic field, which is required in (3), is given in terms of

$$\chi_0(r,r') = -\frac{1}{2\pi}\,{\rm Im}\int_{-\infty}^{E_{\rm F}} \frac{d\omega}{\pi} \sum_{l=0}^{\infty}(2l+1)G_l^+(r,r',\omega)G_l^+(r',r,\omega). \qquad (6)$$

TABLE I. Calculated Knight shifts and related quantities for the Gunnarsson-Lundqvist (Ref. 12) and for the von Barth–Hedin (Ref. 11) (values in brackets) exchange-correlation potentials. All experimental values are taken from Ref. 16 except for Be and Mg which are quoted from Ref. 3.

Metal (r_s)	χ_s (10^{-6} cgs)	$\langle\lvert\psi(0)\rvert^2\rangle_{E_{\rm F}}$	K_s(Eq. 2)	K_s(core)	K_s(valence)	K_s(Eq. 1)	K_s(expt)
Li (3.28)	1.35 (1.18)	27.38	0.0309 (0.027)	-0.0074	0.0348	0.0274 (0.0248)	0.026
Na (3.96)	1.25 (1.04)	152.6	0.160 (0.133)	-0.006	0.137	0.131 (0.117)	0.116
K (4.86)	1.20 (0.95)	339.8	0.343 (0.270)	-0.017	0.271	0.254 (0.219)	0.265
Rb (5.2)	1.20 (0.93)	742.1	0.742 (0.578)	-0.030	0.541	0.511 (0.438)	0.662
Cs (5.64)	1.21 (0.91)	1068	1.05 (0.818)	-0.097	0.891	0.794 (0.659)	1.44
Be (1.88)	1.84 (1.74)	24.88	0.0382 (0.0362)	-0.0085	0.0436	0.0351 (0.0340)	0.0
Mg (2.65)	1.48 (1.35)	125.3	0.155 (0.141)	-0.006	0.143	0.137 (0.129)	0.110
Ca (3.27)	1.35 (1.17)	242.1	0.273 (0.238)	-0.053	0.306	0.253 (0.223)	-
Sr (3.56)	1.29 (1.11)	518.8	0.558 (0.481)	-0.115	0.628	0.513 (0.444)	-
Al (2.06)	1.73 (1.62)	109.6	0.158 (0.149)	-0.008	0.152	0.144 (0.139)	0.164

G_l^+ is obtained as the solution of an appropriate differential equation. The integral in (6) over the negative range of ω leads to a sum of contributions from the occupied core states, while the integral from 0 to E_F gives a continuum contribution. If the continuum part of χ_0 is expressed as $\chi_0^L + \Delta\chi_0$, where χ_0^L is obtained from the Lindhard function, only the few lowest l-values in (6) need be evaluated explicitly to define $\Delta\chi_0$. The integral equation for $m(r)$ obtained from (3) and (4) is then solved by reducing it to a system of linear equations.

The above program has been carried out for a number of simple metals and the calculated Knight shifts are summarized in Table I. We present both the Knight shifts based on (1) with $m(0)$ obtained from the solution of (3) and the values based on the conventional expression (2). The Fermi-surface contact density in the third column is obtained using the self-consistent ionic potentials for the present model. These values are similar to those obtained by Styles and Tranfield[3] for the lighter elements, although significant differences arise for the heavier elements. For example, our value of $\langle|\psi(0)|^2\rangle_{E_F}$ for Cs is only 60% of their value. Since scattering effects appear not to change the contact density in Cs,[3] this discrepancy indicates the importance of achieving self-consistency between the core and valence states in obtaining accurate contact densities, especially for the heavier elements. One should therefore be cautious in accepting calculated contact densities simply on the basis of agreement with experimental Knight-shift values.

The results based on (1) have been partitioned into the core and valence contributions. The former is typically 10% of the latter, and of opposite sign. Interestingly, even an increase in the valence contributions (column 6) over that of column 4 is more than compensated by the negative core contribution, so that a net reduction in the Knight shift is achieved through core polarization. A similar result was observed for the muon.[9] This effect is of opposite sign to that obtained previously for the alkalis[7] although a direct comparison may not be meaningful because of the different formulations.

To explain the source of this core polarization we show in Fig. 1 the core and valence magnetization density and the corresponding effective field defined in Eq. (4) for the representative example of Li. The significant hole in the exchange field in the ion core is due to the suppression of exchange effects by the high core-electron density.

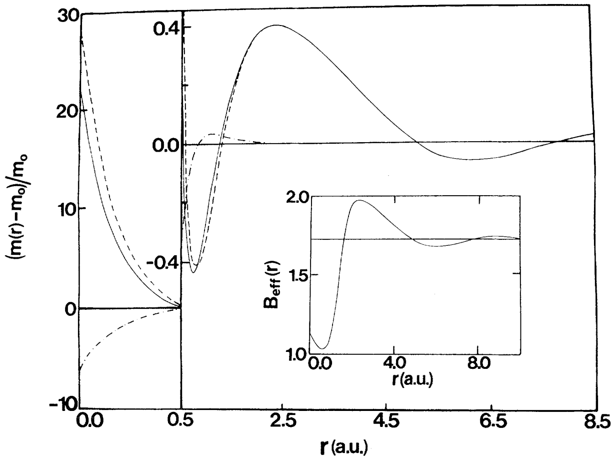

FIG. 1. r dependence of the core (dash-dotted curve), valence (dashed curve), and total (solid curve) magnetization density for Li in units of the background magnetization m_0. Note change in scale at $r = 0.5$ a.u. The inset shows the effective magnetic field in units of the external magnetic field.

In terms of this general feature the core-polarization effects can be given a simple interpretation. Since a uniform field would have no effect on the spatial character of the core states, the hole effectively acts as an inhomogenous magnetic field in a direction *opposite* to that of the applied field and therefore leads to the negative core polarization. However, its effect on the valence states is not predictable; due to the nonlocal character of the continuum part of the response function $\chi_0(r,r')$, a magnetic field localized to the core region can either increase (Li, Be) or decrease (Na, Mg) the valence-state contribution. Within the present formulation it is evident that the conventional expression for the Knight shift (2) corresponds to neglecting the core hole in the exchange field, with instead a uniformly enhanced effective field.

A comparison of our calculated K_s values with experiment[17] shows an overall satisfactory agreement except for Be, Rb, and Cs. The general degree of agreement is similar to that achieved by Styles and Tranfield[3] who used a pseudopotential formulation. The large discrepancy for Be points to the importance of band-structure effects in this metal as evidenced by the unusually small density of states at the Fermi energy.[16] In this case multiple-scattering effects are clearly important and the use of a single-ion Green's function is inadequate. The poor results obtained for Rb and especially Cs suggest the importance in the heavier elements of relativistic effects which we have ignored and which are known to be significant in these metals.[1] Furthermore, one would expect band-structure effects to be relatively more important in the case of Cs. Finally, as a general observation we note that the calculated Knight shift is very nearly a linear function of the nuclear charge Z. To the extent that the experimental values follow this trend it appears that the Knight shift in simple metals is essentially a local property characteristic of a single ion screened by an electron gas.

In conclusion, we have demonstrated an effective method of calculating Knight shifts in simple metals using a linear-response formulation of density functional theory. It should be emphasized that the main virtue of this approach is that, by treating core and valence states in the same way, one can avoid the ambiguous choice of parameters that tends to plague the pseudopotential approach. It also indicates the rather delicate interplay of various important effects, such as core polarization and achieving self-consistency for both the charge and spin densities.

We would like to thank Dr. M. J. Stott for his contributions during the early stages of this work. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

---

[1] S. D. Mahanti, L. Tterlikkis, and T. P. Das, in *Magnetic Resonance*, edited by C. K. Coogan *et al.* (Plenum, New York, 1970).

[2] J. P. Perdew and J. W. Wilkins, Phys. Rev. B 7, 2461 (1973).

[3] G. A. Styles and G. Tranfield, J. Phys. F 8, 2035 (1978).

[4] P. C. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. A1133 (1965).

[5] S. H. Vosko and J. P. Perdew, Can. J. Phys. 53, 1385 (1975).

[6] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1978), 2nd ed.

[7] S. D. Mahanti and T. P. Das, Phys. Rev. B 3, 1599 (1971).

[8] J. F. Janak and A. R. Williams, Phys. Rev. B 14, 4199 (1976).

[9] R. Munjal and K. Petzinger, Hyperfine Interact. 4, 301 (1978).

[10] P. Jena, K. S. Singwi, and R. M. Nieminen, Phys. Rev. B 17, 301 (1978). Values for the spin enhancement reported in this paper are incorrect; subsequent calculations by these authors are in agreement with Ref. 9.

[11] U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).

[12] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).

[13] M. J. Scott and E. Zaremba, Phys. Rev. A, to be published.

[14] J. L. Beeby, Proc. Roy. Soc. London, Ser. A 302, 113 (1967).

[15] M. Manninen, R. Nieminen, P. Hautojärvi, and J. Arponen, Phys. Rev. B 12, 4012 (1975).

[16] See, e.g., J. F. Janak, Phys. Rev. B 16, 255 (1977).

[17] J. M. Titman, Phys. Rep. 33, 1 (1977).

Rare-Earth Magnetic Isolation and Superconductivity of the Chevrel-Phase Compounds

T. Jarlborg
Physics Department and Materials Research Center, Northwestern University, Evanston, Illinois 60201

and

A. J. Freeman
Physics Department and Materials Research Center, Northwestern University, Evanston, Illinois 60201, and Argonne National Laboratory, Argonne, Illinois 60439

(Received 16 October 1979)

Results of *ab initio* self-consistent linear muffin-tin orbital energy-band studies for $EuMo_6S_8$, $GdMo_6S_8$, $SnMo_6S_8$, and $SnMo_6Se_8$ including all electrons in all 15 atoms/unit cell are reported. The large charge transfer from both the Eu, Gd, and Sn sites and from the Mo sites to the chalcogens is shown to be the driving mechanism with which to explain their unusual magnetic and superconducting properties.

The unusual magnetic and superconducting properties of the ternary molydenum chalcogenides have attracted a great amount of experimental and theoretical interest.[1] These Chevrel-phase compounds, with general formula $M_xMo_6S_8$ (or Se_8) and x between 1 and 4, occur for a large