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Abstract. We calculate the Knight shifts, $K(V)$, and spin susceptibilities of the light alkalines Na and Li in the frame of the spin density functional theory (SDA) in the volume range covered by the experiments of Bertani *et al*. All contributions to K have been evaluated rigorously using the data of self-consistent KKR-band-structure calculations. Whereas for Li we get reasonable agreement with experiment, in the case of Na none of the available exchange correlation potentials, K_{xc}, used in the present work reproduces the minimum of $K(V)$ found in the experiments and we show that moderate changes in K_{xc} would be able to remove this deficiency.

1. Introduction

A great deal of experimental and theoretical work has been devoted to the investigation of the Knight shift, the displacement of the NMR frequency of a nucleus in a condensed system relative to the NMR-frequency of the same nucleus in a diamagnetic reference compound. This frequency shift is caused by the interaction between the magnetic moment of the nucleus and the magnetic field induced by the response of the electrons to an external magnetic field. Following the work of Townes *et al* (1950) who tried to interpret the experiments solely in terms of valence electron quantities at the Fermi energy, the theory of this phenomenon has been worked out subsequently in more detail: in connection with their work on Li, Cohen *et al* (1959) and also Gaspari *et al* (1964) pointed out the significance of the core polarization contribution to the hyperfine Hamiltonian. In systems with non-cubic symmetry there exists a contribution due to the spin–dipole interaction (Carter *et al* 1977). The importance of the orbital contribution, K_{orb}, has been recognized by Das and Sondheimer (1960). They showed that in the case of a homogeneous electron gas, K_{orb} is proportional to the Landau diamagnetism and used this term to explain the Knight shift of Be. While the equivalent expressions for K_{orb}, due to Stephen (1962) and Hebborn (1962) and derived by considering the orbital shielding of a nucleus in a metal, are extremely hard to evaluate, Ebert *et al* (1986) gave a tractable prescription for the evaluation of K_{orb} based upon a formula for the orbital susceptibility, χ_{orb}, by Benkowitsch and Winter (1983).

At present, a formulation in the framework of the local spin density functional theory (LSDA) is at hand, expressing all contributions to K in terms of band-structure quantities and potentials derived from LSDA. It is applicable to the whole range of metallic densities.

The results of Ebert *et al* (1986) for some transition metals reveal the importance of K_{orb} and the tendency of the core polarization contribution, K_{cp}, to cancel the term K_s, due to the spin polarization of the valence electrons. The situation is likely to be different in simple metals where s- and p-electrons play the main role and the electronic densities are considerably lower.

The present paper is devoted to a theoretical study of the Knight shift of the light alkalines Na and Li for the wide volume range recently investigated experimentally by Bertani *et al* (1990) and is organized as follows: in section 2 we collect the relevant formulae giving a more detailed account of K_{orb} since in contrast to the work of Ebert *et al* (1986) we avoid any cluster approximation in the evaluation of this term. Section 3 introduces and characterizes the potentials, K_{xc}, used to describe enhancement effects and derived from the various exchange–correlation energy functionals available from literature. The main features of the volume dependent band-structures of Na and Li will be presented in section 4 of this work. The results for the volume-dependent Knight shift and the volume-dependent susceptibility, including a detailed discussion, are given in section 5 and we close with a brief summary.

2. Formalism

Neglecting spin–orbit coupling, the Knight shift, K, may be written as the sum of a spin contribution, K_{spin}, and an orbital part, K_{orb}. We use K_{spin} in the following form used for example by Ebert *et al* (1986)

$$K_{spin} = (8\pi/3)|m(0)|/|B|. \tag{2.1}$$

Here, $m(0)$ is the spin–magnetization density at the nuclear position caused by the homogeneous external field B. In linear response, the relation between the Fourier component, $B(q, \omega)$, of an external magnetic field and the induced spin density, $m(\rho, \omega)$, involves the lattice Fourier transform, χ_q, of the spin–spin correlation function. It reads

$$m(\rho, \omega) = \int d\rho' \, \chi_q(\rho, \rho'; \omega) \, e^{iq\rho'} \, B(q, \omega). \tag{2.2}$$

Here, the coordinates ρ, ρ' are restricted to one unit cell. In a SDA–RPA approximation we evaluate χ_q by setting up and solving the following integral equation (Stenzel and Winter 1985, 1986)

$$\chi_q(\rho, \rho'; \omega) = \chi_q^p(\rho, \rho'; \omega) + \int d\rho_1 \, d\rho_2 \, \chi_q^p(\rho, \rho_1; \omega) K_{xc}(\rho_1, \rho_2) \chi_q(\rho_2, \rho'; \omega). \tag{2.3}$$

While the non-interacting susceptibility, χ_q^p, occurring in (2.3) is evaluated using the calculated KKR-band-structure, the kernel, K_{xc}, is given by the second derivative of the LSDA exchange–correlation energy with repect to the magnetization density (Vosko and Perdew 1975)

$$K_{xc}(\rho, \rho') = \{\delta^2 E_{xc}[n(\bar{\rho}), |m(\bar{\rho})|]/\delta|m(\rho)||\delta m(\rho')|\}|_{|m|=0}. \tag{2.4}$$

Inserting (2.2) into (2.1) we finally obtain for K_{spin}

$$K_{spin} = \frac{8\pi}{3} \lim_{q \to 0} \int d\rho' \, \chi_q(0, \rho'; 0) \, e^{iq\rho'}. \tag{2.5}$$

In our practical applications we evaluate only the valence electron contributions, K_s, to K_{spin} by using the formalism outlined above. The core electron contribution, K_{cp}, on the other hand, is obtained with the help of the following formula (Ebert *et al* 1986)

$$K_{cp} = \frac{8\pi}{3} \mu_B \frac{1}{|B|} \left(\sum_n |\Psi_{ns\uparrow}(0)|^2 - |\Psi_{ns\downarrow}(0)|^2 \right). \tag{2.6}$$

The sum in (2.6) extends over all core states whose amplitudes at the nuclei are spin-dependent due to their interaction with the external field and the spin polarized valence electrons.

To evaluate the orbital contribution, we start with the following relation

$$K_{orb} = \frac{-1}{c\hbar Y_n |B|} \int d\rho \, A_n(\rho) j(\rho) \tag{2.7}$$

with Y_n the gyromagnetic ratio, $A_n = \mu_n \times \rho/\rho^3$ the vector potential of the nuclear magnetic moment and j the orbital current induced by B. The orbital current density $j(\rho, \omega)$ created by the Fourier component $A(q, \omega)$ of an external vector potential reads

$$j_a(\rho, \omega) = \sum_\beta \int d\rho' \, D_q^{\alpha\beta}(\rho, \rho'; \omega) \, e^{iq\rho'} A_\beta(q, \omega). \tag{2.8}$$

Inserting (2.8) into (2.7) we obtain

$$K_{orb} = \frac{-1}{c\hbar Y_n} \lim_{q\to 0} \sum_{\alpha,\beta} \int d\rho \int d\rho' \, e^{iq\rho'} A_{n\alpha}(\rho) D_q^{\alpha\beta}(\rho, \rho'; 0) \frac{A_\beta(q, 0)}{|B|}. \tag{2.9}$$

In our applications we choose B in the y- and q in the z-directions and obtain the following relation

$$K_{orb} = -\frac{1}{c} \int d\rho \int d\rho' \, \frac{z'}{\rho^3} \left(z D_0^{zx}(\rho, \rho'; 0) - x D_0^{zx}(\rho, \rho'; 0) \right) \frac{e^{iqz'}}{q}. \tag{2.10}$$

Instead of employing any cluster approximation as in the work of Ebert *et al* (1986) we express $D^{\alpha\beta}$ in terms of the lattice transform of the one particle Green's function, $g_k(\rho, \rho'; \omega)$, in a similar way as derived for the orbital susceptibility by Götz and Winter (1989). We obtain

$$D_0^{\alpha\beta}(\rho, \rho'; \omega) = D_0^{\alpha\beta\,para} + D^{\alpha\,dia}$$

$$= \frac{-2}{\pi} \int \frac{dk}{\Omega_{BZ}} \, d\varepsilon \, f(\varepsilon) \lim_{\rho_1\to\rho} \lim_{\rho_1'\to\rho'} \left[\left(\frac{\partial}{\partial\rho_\alpha} - \frac{\partial}{\partial\rho_{1\alpha}} \right) \right.$$

$$\times \left(\frac{\partial}{\partial\rho_\beta'} - \frac{\partial}{\partial\rho_{1\beta}'} \right) Im(g_k(\rho, \rho'; \varepsilon) g_k(\rho_1', \rho_1; \varepsilon)) \right]$$

$$- \frac{4}{\pi} Im \int \frac{dk}{\Omega_{BZ}} \int d\varepsilon \, f(\varepsilon) \, Im \, g_k(\rho, \rho'; \varepsilon) \delta(\rho - \rho'). \tag{2.11}$$

In (2.11) only the valence electrons contribute to the paramagnetic part of the correlation function $D_0^{\alpha\beta}(\rho, \rho; \omega)$ leading to $K_{orb}^{para\,val}$. To $D^{\alpha\,dia}$, however, both the core electrons $(K_{orb}^{dia\,core})$ and the valence electrons $(K_{orb}^{dia\,val})$ contribute. Assuming that the core charge densities of the reference compound and the metal are the same, only $K_{orb}^{dia\,val}$ has to be considered in the calculation of K.

In our applications we calculate $\operatorname{Im} D_0^{\alpha\beta}(\rho, \rho'; \omega)$ directly whereas $\operatorname{Re} D_0^{\alpha\beta}(\rho, \rho'; 0)$ is obtained by applying the Kramers–Kronig relation. The inclusion of 24 bands guarantees converged results.

3. Choice of the exchange correlation potential

In contrast to the bandstructure, the spin part of K turned out to depend sensitively on the approximation to the exchange–correlation energy, E_{xc}, used, an observation which is hardly surprising since according to (2.3) the second derivative of E_{xc} with respect to the magnetization density enters the theory of K_{spin}. In the following we give a short compilation of the different expressions for E_{xc} which lead to the different K_{xc} used in the present work. For a more detailed discussion we refer the reader to the original papers.

The local functionals are of the form

$$E_{xc}[n, m] = \int dr\, n(r)\varepsilon_{xc}(n(r), m(r)) \tag{3.1}$$

with $\varepsilon_{xc} = \varepsilon_x(n, \zeta) + \varepsilon_c(n, \zeta)$ and $\zeta = |m|/n$ the relative magnetization. They differ in the approximation to the correlation part ε_c.

Von Barth and Hedin (1972) (vBH) calculated $\varepsilon_c(r_s, \zeta)$ for a number of densities $(n^{-1} = 4\pi/3r_s^3)$ in the metallic range and some values of ζ. Their applications are based on a RPA-type of approximation for the dielectric function. They gave the following parametrization of their results

$$\varepsilon_c(r_s, \zeta) = \varepsilon_c^{vBH}(r_s, 0) + [\varepsilon_c^{vBH}(r_s, 1) - \varepsilon_c^{vBH}(r_s, 0)]f(\zeta) \tag{3.2}$$

with $\varepsilon_c^{vBH}(r_s, 1/0) = -c^{F/P}G(r_s/r^{F/P})$ and $G(x) = (1 + x^3)\ln(1 + 1/x) - x^2 + x/2 - \frac{1}{3}$. Both Janak *et al* (1975) (JMW) and Gunnarsson and Lundqvist (1976) (GL) and also Rajagopal (1980) (R) who go beyond the RPA end up with the same functional form, but their parameters $c^{F/P}$ and $r^{F/P}$ are somewhat different.

We also used the expressions given by Perdew and Zunger (1981) (PZ) and Vosko *et al* (1980) (VWN). They are based on the Monte Carlo results of Ceperley and Alder (1980) (CA) for $\varepsilon_c(r_s, 1)$ and $\varepsilon_c(r_s, 0)$, respectively, at some values for r_s. PZ and VWN derive interpolation formulae for these quantities approaching the correct high density limit as well. To describe the situation of partial magnetization, PZ use the following approximate relation analogous to (3.2).

$$\varepsilon_c^{PZ}(r_s, \zeta) = \varepsilon_c^{CA}(r_s, 0) + [\varepsilon_c^{CA}(r_s, 1) - \varepsilon_c^{CA}(r_s, 0)]f(\zeta). \tag{3.3}$$

The derivation of $\varepsilon_c^{VWN}(r_s, \zeta)$ is more delicate, but both $\varepsilon_c^{VWN}(r_s, \zeta)$ and $\varepsilon_c^{PZ}(r_s, \zeta)$ are somewhat uncertain due to the lack of Monte-Carlo results for partial magnetizations.

In our application of a non-local potential, K_{xc}^{nl}, we followed the lines of Geldart and Taylor (1970a, b) (GT) approximating $K_{xc}(\rho, \rho')$ by its value $K_{xc}^h(\bar{n}, |\rho - \rho'|)$ for a homogeneous electron gas of density $\bar{n} = \frac{1}{2}(n(\rho) + n(\rho'))$ whose Fourier transform, $K_{xc}^h(\bar{n}, |q|)$ and $\chi^P(\bar{n}, |q|)$ are related to the interacting and non-interacting susceptibilities $\chi(\bar{n}, |q|)$ and $\chi^P(\bar{n}, |q|)$, respectively by the following relation

$$K_{xc}^h(n, |q|) = \chi^P(n, |q|)^{-1} - \chi(n, |q|)^{-1}. \tag{3.4}$$

We approximated χ^P and χ by the same diagram as Geldart and Taylor. For comparison we also probed the local limit by replacing $K_{xc}^{GT}(\bar{n}, |q|)$ with $K_{xc}^{GT}(\bar{n}, 0)$.
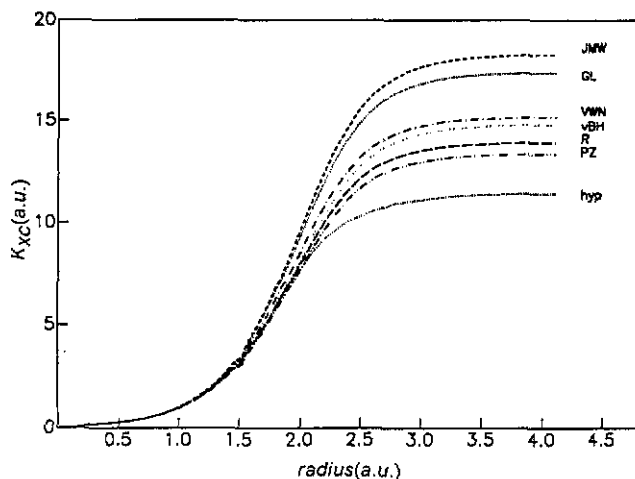
Figure 1. The radial dependence of some of the K_{xc}s presented in section 3 for Na at zero pressure. The potential K_{xc}^{hyp} will be introduced in section 5.

In a series of papers, an extension of the LSDA has been worked out (Langreth and Perdew 1977, 1980) which is based on a modified gradient expansion removing the shortcomings of the gradient expansion originally proposed by Hohenberg and Kohn (1964). In various applications this formulation leads to major improvements in the description of non-magnetic as well as magnetic groundstate properties (Bagno *et al* 1989). We worked with the two potentials K_{xc}^{LMH} and K_{xc}^{PW} derived according to (2.4) from the expressions for E_{xc} given by Langreth and Mehl (1983) and Hu and Langreth (1985) and Perdew (1986a, b) and Perdew and Wang (1986), respectively.

For illustration we show the radial dependencies of the potentials, K_{xc}, within the Wigner–Seitz sphere resulting for some of the approximations described above, for sodium in figure 1 and for lithium in figure 2. These figures show that the potentials
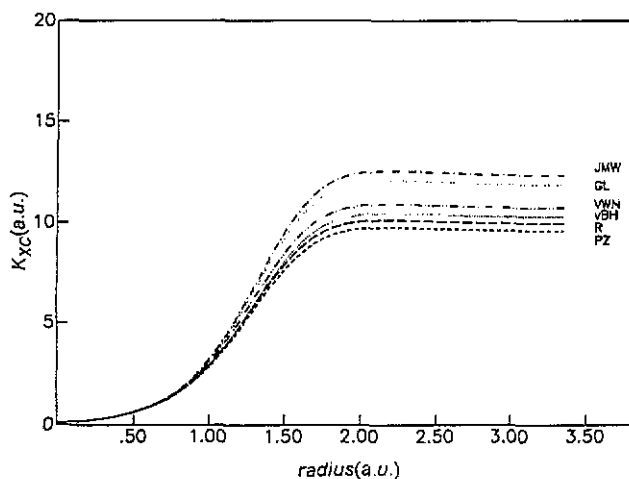

Figure 2. The radial dependence of some of the K_{xc}s presented in section 3 for Li at zero pressure.

obtained with the various approaches differ substantially, especially near the ws–sphere boundary. In the case of sodium which has the lower electronic density these variations are more pronounced than in the case of lithium.

Whereas all the other potentials increase monotonically as a function of the local values of r_s, the K_{xc}s derived from the modified gradient expansions show a pronounced maximum in the range where the core charge density falls to zero and the valence electron density starts to dominate. This feature is caused by the dependence of this kind of potential, K_{xc}, on both the first and the second derivative of the charge density.

4. Features of the volume dependent band structure

We performed self-consistent KKR-band-structure calculations for Na and Li at some lattice constants (column 1 of table 1(2) for Na(Li)) in the pressure range covered by the experiments of Bertani *et al* (1990), and yielding the energies and state-vectors of the 24 lowest valence bands. In all cases concerning Na the occupied part of the lowest bands is of parabolic shape. The DOS, $n(\varepsilon)$, is dominated by s(n_0)- and p(n_1)-partial DOS contributions. Also, a non-negligible d-admixture (n_2) exists. Tables 1 and 2 show these quantities at the Fermi energy (ε_F). In the case of Na the occupied part of the valence band, and also ε_F and $n(\varepsilon_F)$ show jellium-like behaviour. ε_F increases, whereas $n(\varepsilon_F)$ decreases monotonically with decreasing volume. These relations are—also quantitatively—reasonably well described by the formulae of the jellium model

$$\varepsilon_F = (3\pi^2)^{2/3}\Omega_{WS}^{-2/3} \tag{4.1}$$

$$n(\varepsilon_F) = [(3\pi^2)^{1/3}/2\pi^2]\Omega_{WS}^{2/3} \tag{4.2}$$

with Ω_{WS} the volume of the ws-cell.

However, as can be already deduced from the partial DOS, the electron-state vectors deviate markedly from plane waves. This observation applies to both the Bloch coefficients and the radial parts, $R_l(\rho;\varepsilon)$ of the single-site wave functions. The value of $R_0^2(0;\varepsilon_F)$ which turns out to be crucial for the magnitude of K_s is given in column 9 of tables 1 and 2. It rises monotonically with decreasing volume.

In the case of Li the occupied part deviates significantly from a jellium-like behaviour in all respects: the differences to a parabolic band shape and also the anisotropies are non-negligible, $n(\varepsilon_F)$ depends non-monotonically on the volume and the features at ε_F are structure dependent (volumes 1 to 3 of table 2 refer to the BCC-structure, whereas row 4 refers to the FCC-structure). As can be seen from column 9 of table 2 $R_s^2(0;\varepsilon_F)$ increases slightly with pressure in the BCC-phase.

The higher bands and state vectors of these substances which are needed for the calculation of K_{orb} (2.11) do not show any resemblance to plane waves and cannot be approximated by resorting to any model.

Table 1. Volume dependent band-structure quantities for Na.

a	V/V_0	ε_F	$n(\varepsilon_F)$	$n_0(\varepsilon_F)$	$n_1(\varepsilon_F)$	$n_2(\varepsilon_F)$	$n_3(\varepsilon_F)$	$R_0^2(0;\varepsilon_F)$
8.126	1.00	0.2164	6.569	2.630	3.283	0.608	0.048	18.228
7.8456	0.90	0.2451	6.196	2.386	3.176	0.586	0.048	19.292
7.600	0.82	0.2716	5.866	2.203	3.052	0.566	0.045	20.962
7.0391	0.65	0.3499	5.176	1.825	2.782	0.527	0.042	24.920

Table 2. Volume dependent band structure quantities for Li.

a	V/V_0	ε_F	$n(\varepsilon_F)$	$n_0(\varepsilon_F)$	$n_1(\varepsilon_F)$	$n_2(\varepsilon_F)$	$n_3(\varepsilon_F)$	$R_0^2(0; \varepsilon_F)$
6.6338	1.00	0.2961	6.965	1.504	4.997	0.401	0.063	6.243
6.4984	0.94	0.3152	6.402	1.522	4.471	0.357	0.052	6.547
6.1255	0.79	0.3641	6.948	1.259	5.255	0.361	0.073	7.215
7.4964	0.72	0.3719	6.144	1.199	4.563	0.329	0.053	8.356

5. Results and discussion

5.1. Na

In table 3 we collect our results for $K(V)$ and $K_{rel}(V) = K(V)/K(V_0)$. These quantities are indexed according to the potential, K_{xc}, used in their computation. The values of the individual terms defined in section 2 are also given. It is obvious that the spin contribution, K_s, of the valence electron dominates K_{cp} and K_{orb} in the whole volume range. This is the case for both K and K_{rel}. As already suggested by figure 1, table 3 confirms the strong dependence of the results on K_{xc}. As a common feature we observe a monotonic decrease of K_{rel} with decreasing volume, smoothening at higher pressures. Its magnitude, however, varies considerably between the highest value provided by K_{xc}^{PZ} and K_{xc}^{GT} on the one side and the lowest value which is due to K_{xc}^{JMW}. The differences between the absolute values, $K(V_0)$, are still more pronounced: $K^{LMH}(V_0)$, for example, is about 30% above $K^{PZ}(V_0)$ and $K^{GT}(V_0)$. All the calculated values of $K_{rel}(V)$ fall below the experimental results of Bertani *et al* (1990) and fail to reproduce the minimum at $V/V_0 = 0.84$ found by these authors. K_{xc}^{PZ} and K_{xc}^{GT} lead to the best results with respect to both $K(V_0)$ and $K_{rel}(V)$, whereby $K(V_0)$ is about 15% above the experimental number. We extended our calculations to the spin susceptibility, χ, and the numbers for $\chi_{rel}(V) = \chi(V)/\chi(V_0)$ are displayed in column 9 of table 3. Whilst all the potentials, K_{xc}, yield a steep increase of different magnitude at high pressures, the slopes of χ_{rel} at small volume changes vary even in sign. Our low pressure values (e.g. $\chi_{rel}^{PZ}(0.9) = 1.01$) lie below the experimental data of Kushida *et al* (1976) ($\chi_{rel}(0.9) = 1.033$) while no experimental investigations of χ in the high pressure regime are known to us.

The results of table 3 may be compared to other theoretical work. Manninen and Jena (1980) calculated $K_s(V)$ in the range of small pressures for a Na ion immersed into a Fermi sea of a homogeneous electron gas. The deviations of their $K_s(V)$ from experiment are similar to ours. Wilk and Vosko (1981) take account of the band-structure by evaluating the effect of an external magnetic field on the bands and the wave-vectors in the first order. In accordance with us they find that the spin contribution, K_s, dominates and also their $K(V)/K(V_0)$ is close to our value derived from K_{xc}^{VWN}. On the other hand, their $K(V_0)$ is near to experiment. As these authors give no details on their band-structure data, a more precise comparison is impossible.

Our results for K_s may be made more transparent with the help of the following simplified formula (Moruzzi *et al* 1978)

$$K_s = (8\pi/3)Sn_s(\varepsilon_F)R_s^2(0; \varepsilon_F) \tag{5.1}$$

with S the Stonerenhancement, $n_s(\varepsilon_F)$ the partial s-DOS and $R_s(0; \varepsilon_F)$ the radial part of the single-site s-wave function at the nucleus. It reproduces the numbers of table 3 roughly. Whereas, R_s^2 increases almost linearly with pressure, the factor Sn_s decreases

Table 3. Results for the different contributions to the Knight shift of Na as a function of reduced volume for the potentials presented in section 3 (all values in %). K_{xc}^{hyp} will be introduced in section 5. Also the quantities $K_{rel}(V) = K(V)/K(V_0)$ and $\chi_s(V)/\chi_s(V_0)$ are listed.

Potential	a	V/V_0	K	K_{rel}	K_s	K_{cp}	$K_{orb}^{dia\,val}$	$K_{orb}^{para\,val}$	χ_{rel}
GL	8.126	1.00	0.1495	1.000	0.1528	−0.0032	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1418	0.948	0.1451	−0.0032	-0.71×10^{-3}	0.60×10^{-3}	0.999
	7.600	0.82	0.1394	0.932	0.1428	−0.0033	-0.74×10^{-3}	0.63×10^{-3}	1.052
	7.0391	0.65	0.1343	0.898	0.1379	−0.0035	-0.81×10^{-3}	0.71×10^{-3}	1.124
GT	8.126	1.00	0.1327	1.000	0.1345	−0.0017	-0.69×10^{-3}	0.57×10^{-3}	1.000
(local)	7.8456	0.90	0.1274	0.960	0.1293	−0.0018	-0.71×10^{-3}	0.60×10^{-3}	1.013
	7.600	0.82	0.1261	0.950	0.1281	−0.0019	-0.74×10^{-3}	0.63×10^{-3}	1.073
	7.0391	0.65	0.1236	0.931	0.1259	−0.0022	-0.81×10^{-3}	0.71×10^{-3}	1.170
GT	8.126	1.00	0.1311	1.000	0.1329	−0.0017	-0.69×10^{-3}	0.57×10^{-3}	1.000
(non-local)	7.8456	0.90	0.1257	0.959	0.1276	−0.0018	-0.71×10^{-3}	0.60×10^{-3}	1.011
	7.600	0.82	0.1246	0.950	0.1266	−0.0019	-0.74×10^{-3}	0.63×10^{-3}	1.068
	7.0391	0.65	0.1221	0.931	0.1243	−0.0021	-0.81×10^{-3}	0.71×10^{-3}	1.154
JMW	8.126	1.00	0.1541	1.000	0.1578	−0.0036	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1458	0.946	0.1494	−0.0035	-0.71×10^{-3}	0.60×10^{-3}	0.995
	7.600	0.82	0.1429	0.927	0.1467	−0.0037	-0.74×10^{-3}	0.63×10^{-3}	1.046
	7.0391	0.65	0.1371	0.890	0.1410	−0.0038	-0.81×10^{-3}	0.71×10^{-3}	1.111
LMH	8.126	1.00	0.1813	1.000	0.1841	−0.0027	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1731	0.955	0.1760	−0.0028	-0.71×10^{-3}	0.60×10^{-3}	1.009
	7.600	0.82	0.1686	0.930	0.1716	−0.0029	-0.74×10^{-3}	0.63×10^{-3}	1.060
	7.0391	0.65	0.1649	0.910	0.1682	−0.0032	-0.81×10^{-3}	0.71×10^{-3}	1.151
PZ	8.126	1.00	0.1312	1.000	0.1330	−0.0017	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1261	0.961	0.1280	−0.0018	-0.71×10^{-3}	0.60×10^{-3}	1.011
	7.600	0.82	0.1246	0.950	0.1266	−0.0019	-0.74×10^{-3}	0.63×10^{-3}	1.073
	7.0391	0.65	0.1221	0.931	0.1244	−0.0022	-0.81×10^{-3}	0.71×10^{-3}	1.169
R	8.126	1.00	0.1335	1.000	0.1355	−0.0019	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1280	0.959	0.1301	−0.0020	-0.71×10^{-3}	0.60×10^{-3}	1.012
	7.600	0.82	0.1265	0.948	0.1287	−0.0021	-0.74×10^{-3}	0.63×10^{-3}	1.071
	7.0391	0.65	0.1238	0.927	0.1263	−0.0024	-0.81×10^{-3}	0.71×10^{-3}	1.165
vBH	8.126	1.00	0.1370	1.000	0.1392	−0.0021	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1308	0.955	0.1331	−0.0022	-0.71×10^{-3}	0.60×10^{-3}	1.007
	7.600	0.82	0.1290	0.942	0.1314	−0.0023	-0.74×10^{-3}	0.63×10^{-3}	1.064
	7.0391	0.65	0.1256	0.917	0.1282	−0.0025	-0.81×10^{-3}	0.71×10^{-3}	1.124
VWN	8.126	1.00	0.1390	1.000	0.1412	−0.0021	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1330	0.957	0.1353	−0.0022	-0.71×10^{-3}	0.60×10^{-3}	1.009
	7.600	0.82	0.1314	0.945	0.1338	−0.0023	-0.74×10^{-3}	0.63×10^{-3}	1.067
	7.0391	0.65	0.1282	0.922	0.1308	−0.0025	-0.81×10^{-3}	0.71×10^{-3}	1.155
hyp	8.126	1.00	0.1211	1.000	0.1228	−0.0016	-0.69×10^{-3}	0.57×10^{-3}	1.000
	7.8456	0.90	0.1194	0.986	0.1212	−0.0017	-0.71×10^{-3}	0.60×10^{-3}	1.039
	7.600	0.82	0.1192	0.984	0.1211	−0.0018	-0.74×10^{-3}	0.63×10^{-3}	1.111
	7.0391	0.65	0.1212	1.001	0.1235	−0.0022	-0.81×10^{-3}	0.71×10^{-3}	1.257

fast enough to cause the negative slope of K_s in the whole volume range. The high sensitivity of K_s upon changes in the potential K_{xc}, is due to the occurrence of the factor S in (5.1). Because the number for $K_s(V_0)$, (0.1384), obtained by Moruzzi *et al* (1978) using the lattice constant $a = 7.7$ au is comparable to ours (referring to $a = 7.6$ au) and the APW-bandstructure calculations of Papaconstantopoulos (1986) for zero pressure agree with our KKR-results with respect to ε_F and $n(\varepsilon_F)$ while their $n_s(\varepsilon_F)$ is somewhat higher, our band-structure data cannot be blamed for the theoretical overestimation of the experimental value of $K_s(V_0)$. Also, relativistic effects (Tterlikkis *et al* 1969) which turned out to be important for the heavier alkalines (changes of 50% in K_s for Cs) and non-negligible in the case of Rb (~5%) should be unimportant for Na. In view of the large differences between the results obtained with the various available potentials, K_{xc}, and the discrepancies to the experiment it may be worthwhile investigating the changes of K_{xc} necessary to get better agreement. In this connection it is important to remark that both S and the matrix elements of K_{xc}, entering the exact RPA-LSDA formalism are determined by the weakly space-dependent part of $K_{xc}(\rho)$ in the outer region of the WS-sphere, a feature that is due to the dominance of s- and p-type partial waves in the Bloch states. This is in variance with the situation in transition metals where the average electron density is higher and the most important partial waves are of d-character peaking at smaller radii. We introduced the hypothetical potential, K_{xc}^{hyp}, whose values lie somewhat below those of K_{xc}^{PZ}. In the flat part near the WS-sphere boundary and within the pressure range considered ($0.65 \leqslant V/V_0 \leqslant 1$) the relation between K_{xc}^{hyp} and K_{xc}^{PZ} is given by the following formula

$$K_{xc}^{hyp}(\rho, (V/V_0)) = K_{xc}^{PZ}(\rho, (V/V_0))(1 - 0.47((V/V_0) - 0.65)). \quad (5.2)$$

So K_{xc}^{hyp} coincides with K_{xc}^{PZ} at the upper end of the pressure range, where the average electron density comes near to that of Li, while the differences are largest at zero pressure. K_{xc}^{hyp} is also drawn in figure 1. Its deviation from K_{xc}^{PZ} is smaller than the scatter among the other potentials. Our results based on K_{xc}^{hyp} are shown in table 3. $K_{rel}^{hyp}(V)$
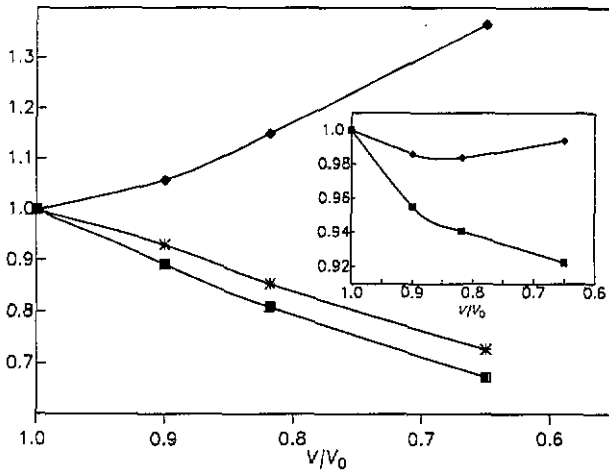

Figure 3. The values of the quantities $X(V) = R_s^2(0, \varepsilon_F; V)/R_s^2(0, \varepsilon_F; V_0)$: ♦ and $Z_1 = S(V)n_s(\varepsilon_F; V)/(S(V_0)n_s(\varepsilon_F; V_0))$: ■ for Na resulting from K_{xc}^{PZ}. The curve marked ∗ shows the latter quantity ($Z_2(V)$) as obtained from the hypothetical potential K_{xc}^{hyp}. Insert: $K_{rel}(V) = X(V)Z_1(V)$: ■ $K_{rel} = X(V)Z_2(V)$: ♦.

agrees with the experiments of Bertani *et al* (1990) and also the absolute values, $K^{hyp}(V)$, show improvement: their overall deviation from experiment has diminished to 7%. Figure 3 illustrates the effect of K_{xc}^{hyp} in terms of the simplified relation according to (5.1): As a consequence of the smoother volume dependence of S the negative slope of n_sS has slightly decreased, leading to an even qualitative change in the behaviour of $K_{rel}(V)$. The use of K_{xc}^{hyp} also yields improvement on the susceptibility data, as a comparison of χ_{rel}^{hyp} (table 3) with the low pressure experiments of Kushida *et al* (1976) shows. Summarizing, we stress that—in contrast to the other potentials—K_{xc}^{hyp} is not really founded from physical grounds. Its purpose is only to illustrate the high sensitivity of $K(V)$ on K_{xc} and to give some idea of the changes to K_{xc} necessary to bring the theoretical results nearer to experiment. Since both K_{xc}^{PZ} and K_{xc}^{VWN} date back to the Monte-Carlo calculations of Ceperley and Alder (1980) performed for the fully spin-polarized and the paramagnetic case only, computations of such a kind for the partly spin-polarized situation would be highly desirable in order to remove possible uncertainties in the corresponding potentials K_{xc}.

5.2. Li

$K(V_0)$, $K_{rel}(V)$ and $\chi_{rel}(V)$ have been evaluated for four lattice constants, the last one referring to the FCC-phase (table 4). In accordance with figure 2 the results show less dependence on K_{xc} than in the case of Na. The maximum difference for $K(V_0)$ occurs between $K^{PZ}(V_0)$ and $K^{JMW}(V_0)$ amounting to 21%. Common to all potentials is a non-linear increase of $K_{rel}(V)$ in the higher pressure regime to numbers around 1.05 and a jump at the transition to the FCC-phase to values near 1. In contrast to Na, besides K_s, K_{cp} contributes non-negligibly to K. It has a negative sign and its magnitude is about $0.2K_s$. Its volume dependence is more pronounced than that of K_s, leading to a significant influence of K_{cp} on $K_{rel}(V)$. K_{orb} on the other hand turns out to be quite small, whereby K_{orb}^{diaval} which has negative sign tends to cancel $K_{orb}^{paraval}$.

In terms of the simplified formula (5.1), which is a poorer approximation to $K(V)$ in the case of Li than for Na, the pronounced increase of $K_{rel}(V)$ is due to the rise of both $R_s^2(0; \varepsilon_F)$ and S. These factors would lead to $K_{rel}(0.79) \approx 1.1$, a value which is considerably reduced by the volume dependence of K_{cp}. The jump of K_{rel} at the phase transition on the other hand is caused by the smaller values of n_s and S in the FCC-phase, whereas $R_s^2(0; \varepsilon_F)$ is slightly above the number in the BCC-phase. Our results may be compared with calculations based on the model of an ion immersed into a homogeneous electron gas. Zaremba and Zobin (1980) use K_{xc}^{GL} to evaluate $K(V_0)$. Their data for K_s and K_{cp} deviate from ours by 12% and 35%, respectively, whereas—due to compensating effects—$K(V_0)$ deviates only by 6%. The calculations of Manninen and Jena (1980) extending to reduced volumes $V/V_0 = 0.9$ yield a steep decrease of $K_{rel}(K_{rel}(0.9) = 0.95)$ stressing the importance of band-structure effects in this system. Wilk and Vosko (1981) treated volume changes up to $V/V_0 = 0.9$. Their $K_{rel}(0.9)$ using K_{xc}^{VWN} is near to ours, but the initial slope of K_{rel} at $V/V_0 \sim 1$ is slightly negative and $K(V_0)$ falls 9% below our value.

The experiments of Kushida and Murphy (1980) (performed for V/V_0 down to ~0.9) agree with those of Bertani *et al* (1990) with respect to $K(V_0)$, but yield a somewhat smaller initial slope for $K_{rel}(V)$.

Our calculated $K(V_0)$ is near to experiment, $K_{rel}(V)$ follows the curve of Kushida and Murphy (1980) at low pressures and for all potentials, K_{xc}, used, $K_{rel}(V)$ is compatible with the results of Bertani *et al* in the range of higher pressures and within the BCC-phase.

Table 4. Results for the different contributions to the Knight shift of Li as a function of reduced volume for different potentials, K_{xc}.

Potential	a	V/V_0	K	K_{rel}	K_s	K_{cp}	K_{orb}^{diaval}	$K_{orb}^{paraval}$	χ_{rel}
GL	6.6338	1.00	0.028 79	1.000	0.039 08	−0.010 04	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.028 38	0.986	0.038 02	−0.009 45	−0.81 × 10⁻³	0.63 × 10⁻³	1.092
	6.1255	0.79	0.030 20	1.049	0.044 76	−0.014 31	−0.92 × 10⁻³	0.67 × 10⁻³	1.127
	7.4964	0.72	0.028 94	1.005	0.041 60	−0.012 29	−0.90 × 10⁻³	0.54 × 10⁻³	1.027
GT (local)	6.6338	1.000	0.024 76	1.000	0.031 52	−0.006 50	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.024 80	1.002	0.031 14	−0.006 15	−0.81 × 10⁻³	0.63 × 10⁻³	1.076
	6.1255	0.79	0.025 84	1.044	0.035 41	−0.009 32	−0.92 × 10⁻³	0.67 × 10⁻³	1.106
	7.4964	0.72	0.024 83	1.003	0.033 83	−0.008 64	−0.90 × 10⁻³	0.54 × 10⁻³	1.035
GT (non-local)	6.6338	1.00	0.023 83	1.000	0.030 34	−0.006 26	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.023 88	1.002	0.029 99	−0.005 93	−0.81 × 10⁻³	0.63 × 10⁻³	1.056
	6.1255	0.79	0.024 91	1.043	0.033 92	−0.008 76	−0.92 × 10⁻³	0.67 × 10⁻³	1.080
	7.4964	0.72	0.023 86	1.001	0.032 23	−0.008 01	−0.90 × 10⁻³	0.54 × 10⁻³	0.996
JMW	6.6338	1.00	0.029 91	1.000	0.041 14	−0.010 97	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.029 35	0.981	0.039 82	−0.010 28	−0.81 × 10⁻³	0.63 × 10⁻³	1.096
	6.1255	0.79	0.031 46	1.052	0.047 39	−0.015 67	−0.92 × 10⁻³	0.67 × 10⁻³	1.134
	7.4964	0.72	0.030 13	1.007	0.043 62	−0.013 13	−0.90 × 10⁻³	0.54 × 10⁻³	1.023
PZ	6.6338	1.00	0.024 56	1.000	0.031 26	−0.006 45	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.024 67	1.004	0.031 00	−0.006 14	−0.81 × 10⁻³	0.63 × 10⁻³	1.072
	6.1255	0.79	0.025 47	1.037	0.034 92	−0.009 19	−0.92 × 10⁻³	0.67 × 10⁻³	1.110
	7.4964	0.72	0.024 68	1.005	0.033 67	−0.008 62	−0.90 × 10⁻³	0.54 × 10⁻³	1.038
R	6.6338	1.00	0.025 12	1.000	0.032 28	−0.006 91	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.025 17	1.002	0.031 94	−0.006 58	−0.81 × 10⁻³	0.63 × 10⁻³	1.076
	6.1255	0.79	0.026 14	1.041	0.036 26	−0.009 87	−0.92 × 10⁻³	0.67 × 10⁻³	1.106
	7.4964	0.72	0.025 20	1.003	0.034 80	−0.009 23	−0.90 × 10⁻³	0.54 × 10⁻³	1.039
vBH	6.6338	1.00	0.025 72	1.000	0.033 26	−0.007 29	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.025 70	0.999	0.032 80	−0.006 92	−0.81 × 10⁻³	0.63 × 10⁻³	1.073
	6.1255	0.79	0.026 67	1.037	0.037 21	−0.010 29	−0.92 × 10⁻³	0.67 × 10⁻³	1.102
	7.4964	0.72	0.025 99	1.010	0.035 59	−0.009 24	−0.90 × 10⁻³	0.54 × 10⁻³	1.030
VWN	6.6338	1.00	0.026 88	1.000	0.034 75	−0.007 62	−0.84 × 10⁻³	0.59 × 10⁻³	1.000
	6.4984	0.94	0.026 84	0.999	0.034 24	−0.007 21	−0.81 × 10⁻³	0.63 × 10⁻³	1.086
	6.1255	0.79	0.028 33	1.054	0.039 51	−0.010 93	−0.92 × 10⁻³	0.67 × 10⁻³	1.119
	7.4964	0.72	0.026 99	1.004	0.037 45	−0.010 09	−0.90 × 10⁻³	0.54 × 10⁻³	1.040

Also, the jump to lower values of $K_{rel}(V)$ at the phase transition is in qualitative agreement with experiment, but its magnitude is below the data of Bertani *et al*. As a comparison of $K^{GT}(V_0)$ to $K^{GTnl}(V_0)$ shows, non-localities in K_{xc} give rise to changes in the percentage range.

The behaviour of the spin susceptibility is characterized by a steep rise of χ_{rel} at high pressures. Its slope at small compressions lies considerably above the values obtained for K_{rel} and is—especially in the case of χ_{rel}^{VWN} and χ_{rel}^{R}—near to the low pressure experiments of Kushida *et al* (1976) who obtain $\chi_{rel}(0.94) = 1.06$. At the phase transition, the theoretical χ_{rel} jumps from 1.4 to 1.25, an effect which is due to the lower values of $n(\varepsilon_F)$ and S in the FCC-phase. The corresponding results of Wilk *et al* (1979) who calculated χ up to $V/V_0 = 0.9$ using the potentials of Shastry as well as of Keiser and Wu and employing the variational principle to include enhancement effects show the same tendency as ours.

Summarizing, one can say that the general agreement between theory and experiment for Li is better than for Na. In this connection it might be interesting to keep in mind that the electronic density of Li is in a range where the hypothetical potential K_{xc}^{hyp} introduced in our treatment of Na would be identical to K_{xc}^{PZ}.

6. Summary

In this work we calculated the volume dependence of the Knight shifts, K and the spin susceptibilities, χ, of the light alkalines Na and Li for an extended volume range ($V_{min}/V_0 = 0.65$ and 0.72 for Na and Li, respectively). A new formulation of the orbital part, K_{orb}, of the Knight shift has been derived and we evaluated all contributions to K in the frame of the SDA-RPA without introducing further approximations. These kind of investigations turned out to provide a sensitive test on the validity of the RPA and the accuracy of the expressions for the exchange–correlation energy functionals, E_{xc}, especially since the potentials K_{xc} are the second derivatives of E_{xc} with respect to the magnetization density.

In the case of Na the various potentials found in literature deviate appreciably from each other and lead to markedly different results for K and χ. This feature is especially pronounced at low electronic densities. None of the potentials used could explain the minimum of K at medium pressures, observed by Bertani *et al* (1990). The differences among the potentials K_{xc} mainly near the surfaces of the Wigner–Seitz-spheres led us to the conclusion that they might be somewhat uncertain. Moreover, the potential K_{xc}^{PZ} which yields the best results for K is based on the Monte-Carlo calculations of Ceperley and Alder (1980). As these authors treat only the paramagnetic and the ferromagnetic state but not the case of partial magnetization, K_{xc}^{PZ} might be insufficiently accurate. By introducing the hypothetical potential, K_{xc}^{hyp}, we demonstrated that moderate changes of K_{xc} suffice to achieve agreement with experiment. Changes of this magnitude might well result from more accurate derivations of exchange correlation energy functional.

In the case of Li where the electronic density is higher and the various potentials, K_{xc}, show less scatter our results are in reasonable agreement with experiment.

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