A pseudopotential calculation of the Knight shift in simple metals

# A pseudopotential calculation of the Knight shift in simple metals

B Mishra†, L K Das‡, T Sahu§, G S Tripathi§ and P K Misra‖

† Department of Physics, Roma Devi Women's College, Bhubaneswar-751001, Orissa, India
‡ Directorate of Education, Bhubaneswar-751001, Orissa, India
§ Department of Physics, Berhampur University, Berhampur-760007, Orissa, India
‖ Department of Physics, Mesa State College, Grand Junction, Colorado 81502, USA

**Abstract.** We calculate the Knight shift $K$ in simple metals using a general expression for $K$ and pseudopotential techniques. $K$ is expressed as the sum $K = K_s + K_o + K_{so}$, where $K_s$, $K_o$ and $K_{so}$ are the spin, orbital and spin–orbit contributions to the Knight shift, respectively. Many-body and spin–orbit interactions are considered and their importance is emphasized. Metals with different crystal structures are considered. Results of the present calculations are compared with those obtained in some recent works. In contrast to other calculations, we obtain good to excellent agreement with experimental results in most of the cases. A remarkable feature of our results is the explanation of the negative Knight shift in beryllium. The fact that the theory explains the Knight shift in several metals suggests that various important mechanisms are accounted for adequately.

## 1. Introduction

We present a detailed calculation of the Knight shift $K$ in simple metals using a recently derived expression for $K$ by Tripathi *et al* (1981, 1982) and a pseudopotential formalism (Phillips and Kleinman 1959, Harrison 1966). Although the subject has been explored extensively during the last two decades (Tterilikkis *et al* 1969, Mahanti *et al* 1970, Mahanti and Das 1971, Perdew and Wilkins 1973, Styles and Tranfield 1978, Zaremba and Zobin 1980, Manninen and Jena 1980, Wilk *et al* 1981, Nusair *et al* 1981) there still remain unanswered questions. For example, the negative Knight shift of beryllium (Barnaal *et al* 1967, Anderson *et al* 1967) was unexplained for a long time. This was mainly due to the use of the conventional formula for the Knight shift given by Townes *et al* (1950):

$$K_s = \frac{8\pi}{3} \chi_s \langle | \psi_{k_F}(0) |^2 \rangle_{av} \tag{1.1}$$

where $K_s$ is the spin contribution to the Knight shift, $\chi_s$ is the exchange-enhanced spin susceptibility and $\langle \ldots \rangle_{av}$ is the spin density averaged over the Fermi surface. Both $\chi_s$ and spin density are positive quantities. Thus the formula proved inadequate to explain the negative Knight shift. The effects of core polarization (Cohen *et al* 1959, Gaspari *et al* 1964) and electron diamagnetism (Landau 1930) were invoked (Jena *et al* 1968, Gerstner and Cutler 1969) in the past for the possible explanation of this unique result, but without much success. Furthermore, there has been no systematic theory which explains the Knight shift of a large number of metals with diverse characteristics.

Recently Tripathi *et al* (1981, 1982) derived a general theory of the Knight shift in solids including many-body and spin–orbit effects from first principles. Their theory considers all the magnetic hyperfine interactions and is expressed as

$$K = K_s + K_o + K_{so} \tag{1.2}$$

where $K_s$, as mentioned earlier, is the spin contribution to the Knight shift but is distinguished from (1.1) in the sense that it involves the effective $g$-factor instead of $\chi_s$; $K_o$ is the orbital contribution; and $K_{so}$ is the result of the effect of spin–orbit interaction on the orbital motion of Bloch electrons. The effect of spin–orbit interaction on the spin of electrons is taken care of via the effective $g$-factor occurring in $K_s$. The theory was later improved to include the effects of indirect nuclear hyperfine interaction (Tripathi 1985, Tripathi *et al* 1987) and electron–phonon interactions (Tripathi *et al* 1989). While the effect of indirect nuclear hyperfine interaction is not relevant for simple metals, the electron–phonon interaction does not modify the Knight shift significantly.

We report in this paper the results of our calculations of the Knight shift in simple metals using equation (1.2) and a non-local pseudopotential formalism. While brief reports of these calculations were published earlier (Mishra *et al* 1984, 1986), we present here details of these calculations and, in addition, some new results. In section 2 we discuss the non-local model potential used in the calculation. In section 3 we use the wavefunctions obtained following the pseudopotential formalism to evaluate the momentum matrix elements, hyperfine interaction matrix elements, chemical potential and the exchange enhancement parameter occurring in the different contributions to $K$. In section 4 we evaluate the Knight shift and section 5 contains a discussion of our results. Finally, in section 6 we present a brief summary and the concluding remarks of the work.

## 2. Non-local model potential

In the present work the optimized model potential proposed by Shaw (1968) is adopted. The Shaw potential has the advantage over the Ashcroft potential (Ashcroft 1968) in the sense that it lends itself readily to a variational optimization procedure. The condition for optimization gives a direct way to determine the model radii. Furthermore, it is intrinsically both non-local and energy dependent, and is not determined from any experimentally obtained property of the solid or liquid state.

The model potential is regarded as a combination of the bare ion potential and the self-consistent potential of all other electrons. We evaluate the self-consistent potential following Shaw and Harrison (1967), which is determined from the electron density by Poisson's equation. The actual electron density $n(r)$ can be regarded as a sum of two terms, a term $\varphi^*_{nk\rho}(r)\varphi_{nk\rho}(r)$ from the model wavefunction and a contribution from the oscillating part of the real wavefunction localized in the core region. Following Shaw and Harrison (1967), we write

$$n(r) = \sum_{\rho, |k| < k_F} \varphi^*_{nk\rho}(r)\varphi_{nk\rho}(r) + \rho \sum_{R_i} \delta(r - R_i) \tag{2.1}$$

where the depletion hole charge $\rho$ which is taken to reside at the centre of the ion is given by

$$\rho = -\sum_{\rho, |k| < k_F} \int d^3r \, \varphi^*_{nk\rho}(r) \frac{\partial W}{\partial E_k} \varphi_{nk\rho}(r) \tag{2.2}$$

where $W$ is the pseudopotential and $E_k$ is the one-electron energy.

We evaluate the pseudowavefunctions by using degenerate perturbation theory, so that we consider coupled bands. At any point on a Bragg reflection plane there are two states of the same energy which are coupled; on the line of intersection there are three states that are coupled, and where two such lines intersect, four states are coupled. However, in order that the problem can be solved analytically, we consider the case of a general point on the plane so that the unperturbed eigenvalue is doubly degenerate.

We write the pseudopotential in the form

$$W = W^{\circ} + W^{so} \tag{2.3}$$

where $W_{o}$ is the spin-independent part used by Misra and Roth (1969) and $W^{so}$ is the spin–orbit part of the pseudopotential. $W^{so}$ can be written in the same form as Weisz (1966)

$$W^{so} = (1 - P_{c}) \frac{\hbar}{4m^{2}c^{2}} \boldsymbol{\sigma} \times \boldsymbol{\nabla} V \cdot \boldsymbol{p}(1 - P_{c}) \tag{2.4}$$

where $P_{c}$, the projection operator, is given by

$$P_{c} = I^{(s)} \sum_{t} |b_{t}\rangle\langle b_{t}|. \tag{2.5}$$

Here $b_{t}$ and $t = nlk$, are the core functions (without spin) centred upon the ion states and $I^{(s)}$ is the identity operator in the spin space.

The eigenvalue equation can then be written in the form

$$\left(\frac{p^{2}}{2m} + W^{\circ} + W^{so}\right)\varphi = E\varphi \tag{2.6}$$

where $\varphi$ is the smooth part of the wavefunction. First we solve equation (2.6) without $W^{so}$, i.e. we solve the following equation

$$\left(\frac{p^{2}}{2m} + W^{\circ}\right)\varphi = \varepsilon\varphi \tag{2.7}$$

where we treat $W^{\circ}$ as a perturbation. We expand

$$|\varphi\rangle = a_{k}|k\rangle + a_{k+Q}|k + Q\rangle \tag{2.8}$$

where $|k\rangle$ and $|k + Q\rangle$ are plane waves, and ignore for the present the other terms. Here $k$, the reduced wavevector, lies near the zone boundary which bisects the reciprocal lattice vector $Q$. Using the standard techniques of degenerate perturbation theory we obtain the energy eigenvalues:

$$\varepsilon\pm = \tfrac{1}{2}(\varepsilon_{1} + \varepsilon_{2}) \pm \tfrac{1}{2}T(\varepsilon_{2} - \varepsilon_{1}) \tag{2.9}$$

where

$$\varepsilon_{1} = \hbar^{2}k^{2}/2m \qquad \varepsilon_{2} = \hbar^{2}(k + Q)^{2}/2m \tag{2.10}$$

and the energy eigenfunctions:

$$|\varphi_{+}\rangle = N|k\rangle + M|k + Q\rangle \tag{2.11a}$$
$$|\varphi_{-}\rangle = M|k\rangle - N|k + Q\rangle \tag{2.11b}$$

where

$$M = [(T + 1)/2T]^{1/2} \tag{2.12a}$$
$$N = [(T - 1)/2T]^{1/2} \tag{2.12b}$$

and

$$T = (1 + 4|W_{Q}|^{2}/(\varepsilon_{2} - \varepsilon_{1})^{2}). \tag{2.13}$$

We now solve the complete eigenvalue equation (equation (2.6)). In the presence

of the spin–orbit interaction both $\varphi_+$ and $\varphi_-$ are double degenerate with regard to spin states:

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

and the unperturbed states for the two levels (equation (2.9)) are $\varphi_+\alpha$, $\varphi_+\beta$, $\varphi_-\alpha$ and $\varphi_-\beta$. Let $\varphi_{1\uparrow}$, $\varphi_{1\downarrow}$, $\varphi_{2\uparrow}$ and $\varphi_{2\downarrow}$ be the perturbed wavefunctions. Thus each can be expanded as a linear combination of the unperturbed states and we write

$$|\varphi_{1\uparrow}\rangle = a_1|\varphi_-\alpha\rangle + a_2|\varphi_-\beta\rangle + a_3|\varphi_+\alpha\rangle + a_4|\varphi_+\beta\rangle \qquad (2.14a)$$

$$|\varphi_{1\downarrow}\rangle = b_1|\varphi_-\alpha\rangle + b_2|\varphi_-\beta\rangle + b_3|\varphi_+\alpha\rangle + b_4|\varphi_+\beta\rangle \qquad (2.14b)$$

$$|\varphi_{2\uparrow}\rangle = c_1|\varphi_-\alpha\rangle + c_2|\varphi_-\beta\rangle + c_3|\varphi_+\alpha\rangle + c_4|\varphi_+\beta\rangle \qquad (2.14c)$$

and

$$|\varphi_{2\downarrow}\rangle = d_1|\varphi_-\alpha\rangle + d_2|\varphi_-\beta\rangle + d_3|\varphi_+\alpha\rangle + d_4|\varphi_+\beta\rangle. \qquad (2.14d)$$

Substituting equation (2.14a) in equation (2.6), taking inner products with respect to $\varphi_-\alpha$, $\varphi_-\beta$, $\varphi_+\alpha$ and $\varphi_+\beta$ and using the general matrix element of $W^{\text{so}}$ between plane wave states (Weisz 1966),

$$\langle k'\rho' | W^{\text{s-o}} | k\rho \rangle = iS(k - k')\left( -\frac{\hbar^2}{4m^2c^2} W(|k - k'|) + \lambda_p + \lambda_d(k' \cdot k) \right) k \times k' \cdot \boldsymbol{\sigma}_{\rho\rho'} \qquad (2.15)$$

where $\rho$ stands for spin states, we have four simultaneous equations in $a_1$, $a_2$, $a_3$ and $a_4$. For non-trivial solutions we have

$$\begin{vmatrix} (\varepsilon_- - E) & 0 & i\dfrac{\hbar}{m}DF_z & i\dfrac{\hbar}{m}DF_- \\[2mm] 0 & (\varepsilon_- - E) & i\dfrac{\hbar}{m}DF_+ & -i\dfrac{\hbar}{m}DF_z \\[2mm] -i\dfrac{\hbar}{m}DF_z & -i\dfrac{\hbar}{m}DF_- & (\varepsilon_+ - E) & 0 \\[2mm] -i\dfrac{\hbar}{m}DF_+ & i\dfrac{\hbar}{m}DF_z & 0 & (\varepsilon_+ - E) \end{vmatrix} = 0 \qquad (2.16)$$

where

$$F = k \times Q \qquad (2.17)$$

$$F_\pm = F_x \pm iF_y \qquad (2.18)$$

and

$$D = \frac{\hbar}{4mc^2} W_Q S(Q) - \lambda_p \frac{m}{\hbar} S(Q) - \lambda_d \frac{m}{\hbar} S(Q)(k^2 + k \cdot Q). \qquad (2.19)$$

Here $S(Q)$ is the structure factor, and $\lambda_p$ and $\lambda_d$ are positive constants that account for the contribution of core p- and d-states, respectively. In general, the spin orbit parameters $\lambda_p$ and $\lambda_d$ are related to the orthogonality coefficients of OPW formulation and, as a result, depend on $k$. However, it has been shown that in the limit of small $k$, such an

approximation for outermost p and d states hold within one per cent in grey tin at values of wavevectors as large as the Fermi wavevector. Solving equation (2.16), we obtain the eigenvalues

$$E_{1/2} = \tfrac{1}{2}(\varepsilon_1 + \varepsilon_2) \mp \tfrac{1}{2}(\varepsilon_2 - \varepsilon_1)Ty \tag{2.20}$$

where

$$y = (1 + 4\hbar^2 D^2 |F|^2 / m^2 (\varepsilon_2 - \varepsilon_1)^2 T^2)^{1/2}. \tag{2.21}$$

The corresponding wavefunctions are

$$|\varphi_{1\uparrow}\rangle = a|\varphi_-\alpha\rangle - b^* F_z |\varphi_+\alpha\rangle - b^* F_+ |\varphi_+\beta\rangle \tag{2.22a}$$

$$|\varphi_{1\downarrow}\rangle = a|\varphi_-\beta\rangle - b^* F_- |\varphi_+\alpha\rangle - bF_z |\varphi_+\beta\rangle \tag{2.22b}$$

$$|\varphi_{2\uparrow}\rangle = a|\varphi_+\alpha\rangle + bF_z |\varphi_-\alpha\rangle + bF_+ |\varphi_-\beta\rangle \tag{2.22c}$$

and

$$|\varphi_{2\downarrow}\rangle = a|\varphi_+\beta\rangle + bF_- |\varphi_-\alpha\rangle + b^* F_z |\varphi_-\beta\rangle \tag{2.22d}$$

where

$$a = [(y + 1)/2y]^{1/2} \tag{2.23}$$

and

$$b = \mathrm{i}\sqrt{2}\,(\hbar/m)D/[y(y + 1)]^{1/2}(\varepsilon_2 - \varepsilon_1)T. \tag{2.24}$$

Equation (2.1) can then be written as, using equations (2.22a)–(2.22d)

$$n(r) = \sum_{|k|<k_F} [2 + 4(1 - 2a^2)MN \exp(\mathrm{i}\mathbf{Q}\cdot\mathbf{r})] + \rho \sum_{\mathbf{R}_i} \delta(\mathbf{r} - \mathbf{R}_i) \tag{2.25}$$

from which the change in the charge density for a single Bragg reflection is written as

$$\delta n(r, \mathbf{Q}) = n_{\mathbf{Q}} \exp(\mathrm{i}\mathbf{Q}\cdot\mathbf{r}) \tag{2.26}$$

where

$$n_{\mathbf{Q}} = \sum_{|k|<k_F} 4(1 - 2a^2)MN + \rho \sum_{\mathbf{R}_i} \exp(-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_i). \tag{2.27}$$

Using Poisson's equation and the Hubbard–Sham approximation (Hubbard 1957, 1958, Sham 1955) for the exchange–correlation potential, the self-consistent potential of the electron becomes

$$W'_{\mathbf{Q}} = \left(\frac{4\pi e^2}{Q^2} + \chi_{\mathbf{Q}}\right) n_{\mathbf{Q}} \tag{2.28}$$

where $\chi_{\mathbf{Q}} \exp(\mathrm{i}\mathbf{Q}\cdot\mathbf{r})$ is the exchange–correlation potential.

The screened form factor can be written as

$$W_{\mathbf{Q}} = N\langle k + \mathbf{Q}|U_0|k\rangle + W'_{\mathbf{Q}} \tag{2.29}$$

where the bare ion-potential is defined as

$$U_0(r) = -\frac{ze^2}{r} - \sum_{l=0}^{l_0} \theta(R_l - r)\left(A_l - \frac{ze^2}{r}\right)P_l. \tag{2.30}$$

Here $\theta$ is a theta function, $P_l$ is an operator which picks out the $l$th angular momentum

component of the conduction electron wavefunction and $z$ is the ion valency. The summation extends to $l_0$, the highest value of the angular momentum of the core states. In general both the well depth $A_l$ and the radius $R$ depend on $l$ but are related by the optimization condition $A_l = ze^2/R_l$, which ensures that the potential is continuous and the pseudowavefunction is as smooth as possible. From equations (2.29) and (2.30) we obtain

$$W_Q = W_Q^\circ + W_Q' + f(\mathbf{k}, \mathbf{Q}) \tag{2.31}$$

where

$$f(\mathbf{k}, \mathbf{Q}) = -N \sum_{l=0}^{l_0} \langle \mathbf{k} + \mathbf{Q}| \left( A_l - \frac{ze^2}{r} \right) P_l | \mathbf{k} \rangle. \tag{2.32}$$

From equations (2.27), (2.28) and (2.31) and using the expressions for $a$, $M$ and $N$, we write $W_Q$ as

$$W_Q = W_Q^\circ / \varepsilon(\mathbf{Q}) + \{[1 + (Q^2/Q)/4\pi e^2]/\varepsilon(\mathbf{Q})\}(V_{dQ} + g_Q) + f(\mathbf{k}, \mathbf{Q}) \tag{2.33}$$

where

$$\varepsilon(\mathbf{Q}) = 1 + 4 \left( \frac{4\pi e^2}{Q^2} + \chi_Q \right) \sum_{|k| < k_F} \frac{1}{(\varepsilon_2 - \varepsilon_1)} \left( 1 - \frac{2\hbar^2 D^2 |F|^2}{m^2(\varepsilon_2 - \varepsilon_1)^2} \right). \tag{2.34}$$

$V_{dQ}$ is the local potential due to a depletion hole

$$V_{dQ} = (4\pi e^2/Q^2)\rho \tag{2.35}$$

and

$$g_Q = \frac{16\pi e^2}{Q^2} \sum_{|k| < k_F} \frac{f(\mathbf{k}, \mathbf{Q})}{(\varepsilon_2 - \varepsilon_1)} \left( 1 - \frac{2\hbar^2 D^2 |F|^2}{m^2(\varepsilon_2 - \varepsilon_1)^2} \right) \tag{2.36}$$

which gives the screening of the non-local part of the bare ion potential. Further, it may be noted that in deriving equation (2.33), the $k$-dependence of $W_Q^\circ$ has been neglected. $W_Q$ is solved self-consistently.

## 3. Pseudopotential formalism of Knight shift

### 3.1. Evaluation of the matrix elements

In order to evaluate the various contributions to the Knight shift, we need to evaluate first the various matrix elements that occur in the expressions for $K_s$, $K_o$ and $K_{so}$ (Tripathi *et al* 1982). The matrix elements of $\boldsymbol{\pi}$, $\boldsymbol{\sigma}$, $(1/r)$, etc, which occur in these expressions are evaluated by using the pseudowavefunctions obtained in equations (2.22). However, it may be noted that one cannot evaluate the hyperfine matrix elements in a similar manner since the pseudowavefunctions do not estimate correctly the spin-density at the nuclear site. In fact, the effect of the core states is predominant in this case. Hence we use the orthogonalized plane waves (OPWs) to evaluate these hyperfine matrix elements. Following a procedure similar to that outlined to obtain equations (2.22) we write the conduction electron wavefunctions $\psi$ (OPWs) as:

$$|\psi_{1\uparrow}\rangle = a|\psi_-\alpha\rangle - b^* F_z |\psi_+\alpha\rangle - b^* F_+ |\psi_+\beta\rangle \tag{3.1a}$$

$$|\psi_{1\downarrow}\rangle = a|\psi_-\beta\rangle - b^* F_- |\psi_+\alpha\rangle - b F_z |\psi_+\beta\rangle \tag{3.1b}$$

$$|\psi_{2\uparrow}\rangle = a|\psi_+\alpha\rangle + bF_z|\psi_-\alpha\rangle + bF_+|\psi_-\beta\rangle \qquad (3.1c)$$

$$|\psi_{2\downarrow}\rangle = a|\psi_+\beta\rangle + bF_-|\psi_-\alpha\rangle + b^*F_z|\psi_-\beta\rangle \qquad (3.1d)$$

where

$$\psi_\pm(r) = \frac{1}{C_\pm}\left[\varphi_\pm(r) - \sum_{i,t} A_{t\pm}\exp(ik\cdot R_i)b_t(r-R_i)\right]. \qquad (3.2)$$

Here

$$A_{t\pm} = \int b_t^*(r)\varphi_\pm(r)\,dr. \qquad (3.3)$$

$C_+$ and $C_-$ are the normalized constants

$$C_\pm^2 = 1 - \frac{1}{\Omega}|A_{t\pm}|^2 \qquad (3.4)$$

where $\Omega$ is the unit cell volume, the $b_t'$ are the atomic core functions and we sum over all the core states.

The ionic core states and the plane wave states are expressed in terms of the spherical harmonics:

$$b_t(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi) \qquad (3.5)$$

and

$$\exp(ik\cdot r) = 4\pi\sum_{l,m} i^l j_l(kr)Y_{lm}^*(\hat{k})Y_{lm}(\hat{r}). \qquad (3.6)$$

Here $R_{nl}(r)$ are the radial parts of the atomic core functions and $j_l(kr)$ are the spherical Bessel functions. Assuming that the ion core states do not overlap, we have the probability density at the nuclear site $R_s$,

$$|\psi_{k+}(R_s)|^2 = \frac{1}{C_+^2}\left\{M + N - \sum_n R_{n0}(0)[MB_{n0}(|k+Q|) + NB_{n0}(k)]\right\}^2 \qquad (3.7)$$

where

$$C_+^2 = 1 - \frac{4\pi}{\Omega}\sum_{n,l}(2l+1)[N^2 B_{nl}^2(k) + M^2 B_{nl}^2(|k+Q|)$$
$$+ 2MN B_{nl}(k)B_{nl}(|k+Q|)P_l(\cos\delta)] \qquad (3.8)$$

and

$$B_{nl}(k) = \int_0^\infty R_{nl}(r)j_l(kr)r^2\,dr. \qquad (3.9)$$

In equation (3.8) $\delta$ is the angle between $k$ and $k+Q$. Similarly, we obtain

$$|\psi_{k-}(R_s)|^2 = \frac{1}{C_-^2}\left(M - N - \sum_n R_{n0}(0)[MB_{n0}(k) - NB_{n0}(|k+Q|)]\right)^2 \qquad (3.10)$$

where

$$C_-^2 = 1 - \frac{4\pi}{\Omega}\sum_{n,l}(2l+1)[M^2 B_{nl}(k) + N^2 B_{nl}(|k+Q|)$$
$$- 2MN B_{nl}(k)B_{nl}(|k+Q|)P_l(\cos\delta)]. \qquad (3.11)$$

It may be noted that while evaluating the hyperfine matrix elements of the type

$$X^{\nu}_{nk\rho,mk\rho'} = \int \psi^{+}_{nk\rho}(r)X^{\nu}\psi_{mk\rho'}(r)\,\mathrm{d}r \tag{3.12}$$

we have only considered the contact part of the hyperfine interaction. The orbital and dipolar hyperfine interactions are expected to be small for the systems considered.

### 3.2. Evaluation of the chemical potential

The number of electrons per unit volume $n'$ is given by the expression

$$n' = \frac{1}{4\pi^3}\int \mathrm{d}^3k\, f(E_k - \xi) \tag{3.13}$$

where $f(E_k - \xi)$ is the Fermi function, $\xi$ is the chemical potential and $E_k$ is the one-electron energy obtained in equation (2.20). In cylindrical coordinate systems

$$\mathrm{d}^3k = \tfrac{1}{2}\mathrm{d}k_\rho^2\,\mathrm{d}k_z\,\mathrm{d}\varphi \tag{3.14}$$

where $k_\rho^2 = k_x^2 + k_y^2$. Defining $q_z = k_z + Q/2$, equation (3.13) can be written as

$$n' = \frac{1}{4\pi^2}\int \mathrm{d}q_z \int \mathrm{d}k_\rho^2\, f(E_k - \xi). \tag{3.15}$$

Integrating the right-hand side of equation (3.15) by parts and using the fact that at low temperatures $f'(E - \xi) = -\delta(E - \xi)$, we obtain

$$n' = \frac{1}{4\pi^2}\int \mathrm{d}q_z \int k_\rho^2\delta(E- \xi)\,\mathrm{d}E. \tag{3.16}$$

Now integration over $E$ in equation (3.16) causes $k_\rho^2$ to be replaced by

$$k_\rho^2 = -q_z^2 + \delta Q^2 + (p - 1)Q^2/4 + Q(\alpha q_z^2 + \beta Q^2)^{1/2} \tag{3.17}$$

which is obtained by solving $E - \xi = 0$. In equation (3.17)

$$\alpha = 1 - 2\delta \tag{3.18}$$

$$\delta = 2D^2/\hbar^2 \tag{3.19}$$

$$\beta = t^2 + \delta^2 + (p - 1)\delta/2 \tag{3.20}$$

$$t^2 = (4m^2 W_Q^2)/(\hbar^4 Q^4) \tag{3.21}$$

$$p = 8m\xi/(\hbar^2 Q^2). \tag{3.22}$$

Using the $\delta$-function property and the relation

$$\gamma = (2/Q)k_z \tag{3.23}$$

equation (3.16) can be written as

$$n' = \frac{Q^3}{32\pi^2}\int_{\gamma_-}^{\gamma_+} \mathrm{d}\gamma\,[-\gamma^2 + p + 4\delta - 1 \pm 2(\alpha\gamma^2 + 4\beta)^{1/2}] \tag{3.24}$$

where

$$\gamma_\pm = [|1 + p \pm 2(p + 4t^2)^{1/2}|]^{1/2}. \tag{3.25}$$

For $Q > 2k_F$, both $\gamma_+$ and $\gamma_-$ are positive and the integration in equation (3.24) is evaluated taking the positive sign before the square root term. For $Q < 2k_F$, the inte-

gration is separated into two parts; the limit of one is from $\gamma_-$ to 0, in which case we take the negative sign and $\gamma_- = -|1 + p - 2\sqrt{p + 4t^2}|$, and the other is from 0 to $\gamma_+$ in which case we take the positive sign. Further, from the free electron theory

$$n' = \tfrac{4}{3}(Q^3/32\pi^2)p_0^{3/2} \tag{3.26}$$

where

$$p_0 = 8m\xi_0/\hbar^2 Q^2 \tag{3.27}$$

and $\xi_0$ is the free electron Fermi energy. From equations (3.24) and (3.26), we have

$$p = \left(\frac{3}{4}\int_{\gamma_-}^{\gamma_+} [-\gamma^2 + p + 4\delta - 1 + 2(\alpha\gamma^2 + 4\beta)^{1/2}]\,d\gamma\right)^{2/3}. \tag{3.28}$$

Writing the right-hand side as $F(p)$, we write (3.28) in the following form

$$p = p_0 - [F(p) - p]. \tag{3.29}$$

The chemical potential can be evaluated from (3.29) by the process of reiteration.

### 3.3. Evaluation of the exchange enhancement factor

The exchange enhancement factor occurring in $K_s$ is given by (equation (4.20) of Tripathi *et al* (1982))

$$\alpha_n(k) = -\sum_{k'} v_{nn}(k, k')f(E_{nk'}) \tag{3.30}$$

where we have made an intraband interaction approximation and

$$v_{nn}(k, k') = \int \psi_{nk\rho}^*(r)\psi_{nk\rho'}(r')v_{\rm eff}(r, r')\psi_{nk'\rho}(r)\psi_{nk'\rho'}^*(r')\,dr\,dr'. \tag{3.31}$$

We assume the Thomas–Fermi model for the Coulomb potential

$$v_{\rm eff}(r, r') = e^2 \exp(-\lambda|r - r'|)/|r - r'| \tag{3.32}$$

where

$$\lambda = (4me^2/\pi\hbar^3)\sqrt{2m\xi_0}. \tag{3.33}$$

For evaluating $v_{nn}(k, k')$ in (3.32), we do not consider the core states. Hence we use the pseudowavefunctions $\varphi_{nk\rho}$ obtained in (2.22). From (2.22), (3.31) and (3.32), we have

$$v_{nn}(k, k') = \frac{M_1}{|k - k'|^2 + \lambda^2} + \frac{M_2}{|k - k' - Q|^2 + \lambda^2} + \frac{M_3}{|k - k' + Q|^2 + \lambda^2} \tag{3.34}$$

where

$$M_1 = \pi e^2([(1 + X_1)(1 + X_2)]^{1/2} + t^2 X_1 X_2/q_z q_z'[(1 + X_1)(1 + X_2)]^{1/2})^2 \tag{3.35}$$

$$M_2 = \pi e^2(t^2 X_2^2(1 + X_1)/q_z'(1 + X_2)) \tag{3.36}$$

$$M_3 = \pi e^2(t^2 X_1^2(1 + X_2)/q_z(1 + X_1)) \tag{3.37}$$

$$X_1 = q_z/(q_z^2 + t^2)^{1/2} \tag{3.38}$$

$$X_2 = q_z/(q_z'^2 + t^2)^{1/2} \tag{3.39}$$

$$q_z = k_z + Q/2 \tag{3.40}$$

$$q_z' = k_z' + Q/2. \tag{3.41}$$

$\alpha_n(\mathbf{k})$ was evaluated numerically using cylindrical coordinates.

## 4. Evaluation of the Knight shift

The summations over $k$ states occurring in $K_s$, $K_o$ and $K_{so}$ (equations (3.43), (3.44) and (4.21) of Tripathi *et al* (1982)) are evaluated by using the cylindrical coordinate system. Using equations (2.20), (3.23), (3.30) and the $\delta$-function properties, $K_s^{\|(\perp)}(Q)$ can be written as

$$K_s^{\|(\perp)}(\boldsymbol{Q}) = -\frac{1}{8\pi^2}\frac{Q}{2}\int_{\gamma_-}^{\gamma_+} \mathrm{d}\gamma \left(\frac{\mathrm{d}k_\rho^2}{\mathrm{d}E} K_s^{\|(\perp)}(\boldsymbol{Q}, k_\rho^2, \gamma)\right)\bigg|_{k_\rho^2 = F(\gamma)} \tag{4.1}$$

where $F(\gamma)$ is the right-hand side of equation (3.17),

$$\mathrm{d}E/\mathrm{d}k_\rho^2 = \hbar^2/2m + \tfrac{1}{2}A_E B_E Q^2/(1 + B_E Q^2 k_\rho^2)^{1/2} \tag{4.2}$$

$$A_E = -\tfrac{1}{2}(\hbar^2/m^2)T(Q^2 + 2\mathbf{k} \cdot \boldsymbol{Q}) \tag{4.3}$$

$$B_E = 4(\hbar^2/m^2)D^2/[(\varepsilon_2 - \varepsilon_1)^2 + 4|W_Q|^2]. \tag{4.4}$$

In (4.1) the $\|$ and $\perp$ components can be obtained by applying the magnetic field in the $z$-direction and $x$ or $y$ directions, respectively. Similarly, we obtain:

$$K_o^{\|(\perp)}(\boldsymbol{Q}) = \frac{1}{8\pi^2}\frac{Q}{2}\int_{\gamma_-}^{\gamma_+} \left(\int_0^{k_\rho^2} K^{\|(\perp)}(\boldsymbol{Q}, k_\rho^2, \gamma)\,\mathrm{d}k_\rho^2\right)\mathrm{d}\gamma \tag{4.5}$$

$$K_{so}^{\|(\perp)}(\boldsymbol{Q}) = \frac{1}{8\pi^2}\frac{Q}{2}\int_{\gamma_-}^{\gamma_+} \left(\int_0^{k_\rho^2} K^{\|(\perp)}(\boldsymbol{Q}, k_\rho^2, \gamma)\,\mathrm{d}k_\rho^2\right)\mathrm{d}\gamma. \tag{4.6}$$

It may be noted that $K_s(Q)$, $K_o(Q)$ and $K_{so}(Q)$ are the contributions to the Knight shift in the single Bragg reflection case. However, we consider a more realistic case in which a number of Bragg reflections occur, some of which cut the Fermi surface. We shall assume that the different Bragg planes are independent, thereby meaning that we neglect the crossing on the Fermi surface of two or three Bragg planes. This is based on the assumption that the pseudopotential is sufficiently small that we can treat only one Bragg plane at a time to better than the second order.

In order to calculate the contributions from many Bragg reflections, we write $K_s$, $K_o$ and $K_{so}$ in the form

$$K_s^{\|(\perp)} = K_s^f + \sum_Q D_o^{\|(\perp)}(\boldsymbol{Q}) \tag{4.7}$$

$$K_o^{\|(\perp)} = K_o^f + \sum_Q D_o^{\|(\perp)}(\boldsymbol{Q}) \tag{4.8}$$

$$K_{so}^{\|(\perp)} = \sum_Q K_{so}^{\|(\perp)}(\boldsymbol{Q}) \tag{4.9}$$

where $K_s^f$ and $K_o^f$ are the contributions to the Knight shift in the presence of electron–electron interactions but in the absence of both band and spin–orbit effects, and

$$D_s^{\|(\perp)}(\boldsymbol{Q}) = -\frac{Q}{16\pi^2}\int_{\gamma_-}^{\gamma_+} \left[\left(\frac{\mathrm{d}k_\rho^2}{\mathrm{d}E}\right)K_s^{\|(\perp)}(\boldsymbol{Q}, k_\rho^2, \gamma)\right]\mathrm{d}\gamma - K_s^f - \tfrac{1}{3}K_s^f\left(\frac{n'}{n_0'} - 1\right) \tag{4.10}$$

$$D_o^{\|(\perp)}(\boldsymbol{Q}) = \frac{Q}{16\pi^2}\int_{\gamma_-}^{\gamma_+} \left(\int_0^{k_\rho^2} K_o^{\|(\perp)}(\boldsymbol{Q}, k_\rho^2, \gamma)\,\mathrm{d}k_\rho^2\right)\mathrm{d}\gamma - K_o^f - \tfrac{1}{3}K_o^f\left(\frac{n'}{n_0'} - 1\right) \tag{4.11}$$

**Table 1.** Details of the calculations of the Knight shift in alkali metals.

| Metal | $K_s^f$ $(\times 10^{-2})$ | $\Sigma_Q D_s(Q)$ $(\times 10^{-2})$ | $K_o^f$ $(\times 10^{-7})$ | $\Sigma_Q D_o(Q)$ $(\times 10^{-7})$ | $\Sigma QQ D_{so}(Q)$ |
|-------|-----------|--------------|-----------|--------------|--------------|
| Li | 0.051 42 | −0.021 23 | −2.950 | 0.797 | −0.3277 × 10⁻⁹ |
| Na | 0.1172 | −0.017 23 | −1.688 | 0.065 | 0.1136 × 10⁻⁵ |
| K | 0.2888 | 0.0062 | −0.8923 | −0.1317 | 0.1090 × 10⁻⁴ |
| Rb | 0.4991 | 0.0430 | −0.7319 | −0.1889 | 0.1039 × 10⁻³ |
| Cs | 0.9056 | 0.3053 | −0.5757 | −0.3130 | 0.3489 × 10⁻³ |

$$D_{so}^{\|(\perp)}(Q) = \frac{Q}{16\pi^2} \int_{\gamma_-}^{\gamma_+} \left( \int_0^{k_\rho^2} K_{so}^{\|(\perp)}(Q, k_\rho^2, \gamma) \, \mathrm{d}k^2 \right) \mathrm{d}\gamma. \tag{4.12}$$

In (4.10) and (4.11) the last terms are the correction terms due to the inclusion of many-Bragg reflections and are obtained following a procedure similar to the technique followed by Misra *et al* (1971).

Since we are formulating the problem for simple metals we derive expressions for the isotropic and anisotropic components of the Knight shift. It may be noted that even for cubic metals, the spin–orbit interaction makes the Knight shift anisotropic. Thus $K_s$, $K_o$ and $K_{so}$ can be written as

$$K_s = \tfrac{1}{3}K_s^{\|} + \tfrac{2}{3}K_s^{\perp} \tag{4.13}$$

$$K_o = \tfrac{1}{3}K_o^{\|} + \tfrac{2}{3}K_o^{\perp} \tag{4.14}$$

$$K_{so} = \tfrac{1}{3}K_{so}^{\|} + \tfrac{2}{3}K_{so}^{\perp}. \tag{4.15}$$

The Hartree–Fock wavefunctions were used from Clementi's table (Clementi 1968) for metals with atomic numbers less than thirty and from Mann's table (Mann 1968) for other metals.

The non-local pseudopotential $W_Q$ occurs in an involved manner in our expressions for $K$. We write the model potential obtained by us in (2.33) in the form

$$W_Q(k) = W_Q^L + f(k, Q) \tag{4.16}$$

where

$$W_Q^L = (1/\varepsilon(Q))[W_Q^o + (1 + Q^2\lambda_Q/4\pi e^2)(V_{dQ} + g_Q)] \tag{4.17}$$

is the local part of the model potential and is essentially independent of $k$. We have calculated $W_Q$ separately by a reiteration process since both $\varepsilon(Q)$ and $g_Q$ are functions of $W_Q$ as evident from (2.36) and (2.37). The second term $f(k, Q)$ is non-local and consequently retained in the angular integrations. The model potential parameter used in the calculations has been taken from Ese and Reissland (1973), while the values of $\rho$ have been taken from Shaw (1968). The values of $\lambda_p$ and $\lambda_d$ have been calculated following a procedure outlined by Weisz (1966) and using Herman–Skillman atomic functions (Herman and Skillman 1963).

## 5. Results and discussion

We have tabulated our results in tables 1–4. In all the systems studied, the spin contribution to the Knight shift $K_s$ is still the dominant term. However, the importance of $K_{so}$ increases as one goes from the lighter metals to heavier ones. As expected $K_o$ is small in most cases.

**Table 2.** Details of calculations of the Knight shift in divalent HCP and other metals.

| Metal | $K_s^f$ ($\times 10^{-2}$) | $\Sigma_Q D_s(Q)$ ($\times 10^{-2}$) | $K_o^f$ ($\times 10^{-7}$) | $\Sigma_Q D_o(Q)$ ($\times 10^{-7}$) | $\Sigma_Q Q D_{so}(Q)$ |
|---|---|---|---|---|---|
| Be | 0.066 32 | $-0.070\ 76$ | $-0.070\ 72$ | $-0.1566$ |
| Mg | 0.1266 | $-0.020\ 10$ | $-0.021\ 24$ | $-0.055\ 22$ |
| Zn | 0.4589 | $-0.1490$ | $-0.1472$ | $-0.083\ 63$ |
| Al | 0.1249 | 0.0489 | 0.0445 | $-0.1156$ |
| Ga | 0.4353 | $-0.0536$ | $-0.0522$ | $-0.097\ 99$ |

| Metal | $\Sigma_Q D_o^{\parallel}(Q)$ ($\times 10^{-5}$) | $\Sigma_Q D_o^{\perp}(Q)$ ($\times 10^{-5}$) | $\Sigma_Q D_{so}^{\parallel}(Q)$ | $\Sigma_Q D_{so}^{\perp}(Q)$ |
|---|---|---|---|---|
| Be | 0.1044 | 0.1040 | $0.5085 \times 10^{-7}$ | $0.7087 \times 10^{-7}$ |
| Mg | 0.2051 | 0.2046 | $-0.2875 \times 10^{-5}$ | $-0.5217 \times 10^{-5}$ |
| Zn | 0.046 82 | 0.046 86 | $0.1084 \times 10^{-2}$ | $0.1377 \times 10^{-2}$ |
| Al | $-0.1458$ | $-0.0364$ | $0.2662 \times 10^{-4}$ | $0.2659 \times 10^{-4}$ |
| Ga | 0.007 19 | 0.006 88 | $0.6292 \times 10^{-3}$ | $0.1885 \times 10^{-2}$ |

As regards the alkali metals, the agreement of our results with experiment is fairly good. From table 1 it is clearly evident that the band structure effects are important in the Li case, and to some extent in caesium. Sodium, potassium and rubidium behave almost as free-electron-like systems. $K_o$ is much smaller than $K_s$ in all the metals. However, $K_{so}$ is important in heavier metals. Indeed it is of the same order as $K_s$ in the case of Cs. It would be pertinent at this stage to compare our results with some of the recently published theoretical results by Styles and Tranfield (ST) (1978) and Zaremba and Zobin (ZZ) (1980) employing markedly different techniques. While the ST calculations employ a non-local model-potential technique to calculate the spin-density and experimental values of the spin susceptibility, the ZZ technique formulated a linear response theory to calculate the Knight shift in metals based on the density functional formalism (Hohenberg and Kohn 1964, Kohn and Sham 1965). The ST calculations are not self-consistent in the sense that they use experimental values for the spin susceptibility. Further, the quantitative agreement even for a free-electron-like system such as potassium is far from satisfactory. On the other hand, the ZZ calculations give different results for different exchange–correlation potentials. Moreover, in the case of Rb and Cs, their agreement with experiment is poor, and is probably due to the neglect of relativistic effects. In comparison, there is fair agreement of our results with experiment in all the alkali metals.

The remarkability of the present work rests on its success to explain the negative Knight shift in Be. This feat has been achieved due to two important factors: (i) the use of our general theory of Knight shift (Tripathi *et al* 1982) and (ii) the use of a non-local pseudopotential formalism. To elucidate the first point, we emphasize that our $K_s$ value is the result of a first-principles derivation, while the conventional $K_s$ was obtained based on the simplest approximations. The conventional $K_s$ depends on $\chi_s$ and the averaged value of the spin density $\langle |\psi_{K_f}(0)|^2 \rangle_{av}$ at the Fermi surface, and both these quantities are positive. It may be noted that, in the most rigorous analysis, $\chi_s$ is proportional to the square of the effective $g$ factor. In comparison, our $K_s$ depends only on the effective $g$ factor. Therefore, while the dependence of the conventional $K_s$ on $\chi_s$ is linear, it is non-linear in our case. This is a remarkable difference between the conventional $K_s$ and our $K_s$.

Furthermore, while the conventional $K_s$ employs the averaged value of the spin density at the Fermi surface, our $K_s$ involves the summation over all the $k$ states and thus

**Table 3.** Parallel and perpendicular components of $K_s$, $K_o$, $K_{s\text{-}o}$ for divalent and other metals.

| Metals | Structure | $K_s^{\parallel}$ ($\times 10^{-2}$) | $K_s^{\perp}$ ($\times 10^{-2}$) | $K_o^{\parallel}$ ($\times 10^{-5}$) | $K_o^{\perp}$ ($\times 10^{-5}$) | $K_{s\text{-}o}^{\parallel}$ | $K_{s\text{-}o}^{\perp}$ |
|---|---|---|---|---|---|---|---|
| Be | HCP | −0.004 444 | −0.004 399 | −0.052 24 | −0.052 61 | $0.5084 \times 10^{-7}$ | $0.7081 \times 10^{-7}$ |
| Mg | HCP | 0.1020 | 0.1009 | 0.1461 | 0.1456 | $-0.2925 \times 10^{-5}$ | $-0.5296 \times 10^{-5}$ |
| Zn | HCP | 0.3098 | 0.3151 | −0.046 26 | −0.046 21 | $0.1343 \times 10^{-2}$ | $0.1660 \times 10^{-2}$ |
| Al | FCC | 0.1736 | 0.1694 | −0.2614 | −0.1520 | $0.2662 \times 10^{-4}$ | $0.2659 \times 10^{-4}$ |
| Ga | Orthorhombic | 0.3817 | 0.3831 | −0.091 14 | −0.091 14 | $0.6598 \times 10^{-3}$ | $0.1886 \times 10^{-2}$ |

**Table 4.** Results of Knight shift.

| Metal | Structure | $K_s$ ($\times 10^{-2}$) | $K_o$ ($\times 10^{-6}$) | $K_{s\text{-}o}$ | $K_{Th}$ ($\times 10^{-2}$) | $K_{exp}$ ($\times 10^{-2}$) |
|---|---|---|---|---|---|---|
| Li | BCC | 0.030 19 | −0.2153 | $-0.3277 \times 10^{-9}$ | 0.0301 | 0.0249 |
| Na | BCC | 0.099 97 | −0.1623 | $0.1136 \times 10^{-5}$ | 0.1008 | 0.108 |
| K | BCC | 0.2950 | −0.1024 | $0.1090 \times 10^{-4}$ | 0.296 | 0.27 |
| Rb | BCC | 0.5241 | −0.092 08 | $0.1030 \times 10^{-4}$ | 0.534 | 0.648 |
| Cs | BCC | 1.2109 | −0.088 87 | $0.3484 \times 10^{-3}$ | 1.254 | 1.57 |
| Be | HCP | −0.004 414 | −0.5249 | $0.6416 \times 10^{-7}$ | −0.0044 | −0.0026 |
| Mg | HCP | 0.1013 | 1.458 | $0.4505 \times 10^{-5}$ | 0.1010 | 0.110 |
| Zn | HCP | 0.3133 | −0.4623 | $0.1554 \times 10^{-2}$ | 0.4688 | — |
| Al | FCC | 0.1707 | −1.884 | $0.2659 \times 10^{-4}$ | 0.1732 | 0.164 |
| Ga | Orthorhombic | 0.3826 | −0.9114 | $0.1477 \times 10^{-2}$ | 0.5303 | 0.449 |

the actual integration over the Fermi volume. This difference is indeed vital for systems where the band structure effects are important.

It may be noted that Petzinger and Munjal (1977) also considered the entire occupied states in calculating the hyperfine fields at positive muons in Ni. If we analyse the results, it can be easily concluded that the band structure effects are really very important in beryllium. From table 2, it is very clear that while in the case of Mg and Zn, $K_s^f$ is greater than $\Sigma_Q D_s(Q)$, which is due to band effects, in the case of Be the latter is greater than $K_s^{free}$. In all the three cases $K_s^f$ is positive and band effect contributions are negative. Since only in Be the band effect contribution is more than that due to the free electron approximation, the Knight shift in Be becomes negative. As expected, $K_0$ and $K_{so}$ are very small in comparison to $K_s$ in Be. This is in contrast with the Gerstner and Cutler (1969) result which shows that diamagnetism of conduction electrons is responsible for the negative Knight shift in beryllium.

While the orbital contribution is small in all the cases considered, the spin–orbit contribution is found to be important in zinc and gallium. In these cases $K_{so}$ is of the same order as $K_s$. This demonstrates that the spin–orbit contribution is an important factor in explaining the Knight shift in heavier metals. We emphasize that in most cases the agreement with experiment, where available, is fairly good.

## 6. Summary and conclusion

The principal results of this work is obtaining tractable expressions for the various contributions to the Knight shift in metals through the use of pseudopotential formalisms and degenerate perturbation theory. The many-body and spin–orbit effects have been included in the calculations from the beginning in a systematic way. While in the previous calculations of the Knight shift in metals, only the spin contribution to $K$, i.e. $K_s$, has been considered, the present work elucidates for the first time the distinguishability of various contributing mechanisms as separate contributions to the Knight shift.

We have extended the optimized model potential of Shaw to evaluate the non-local pseudopotential by first obtaining the pseudo wavefunctions using degenerate perturbation theory in which the pseudopotential has been treated as a perturbation. In order to evaluate the hyperfine matrix elements occurring in different contributions to $K$, we have constructed the OPWs, where the pseudowavefunctions obtained have been used for the smooth parts of the OPWs. The exchange enhancement parameter and the chemical potential have been calculated through the use of the pseudowavefunctions and the corresponding energies.

It may be noted that in some of the previous calculations of the Knight shift efforts have been made to concentrate on the spin-density part, and the spin-susceptibility has usually been taken from experiments. On the other hand, although calculations based on the spin-density formalism (SDF) have considered both parts, the results are sensitive to the approximations for the exchange and correlation potential. Thus, our calculation, besides being a first principle one, has the added advantage that the self consistency between the hyperfine and crystalline parts has been carefully accounted for.

In conclusion, we believe that in this work we have made a serious effort to calculate the Knight shift in metals in a systematic way. Our calculation, in contrast to other calculations, shows for the first time excellent agreement with experimental results in most of the metals chosen for the calculations. The fact that the present formalism works well for systems with diverse characteristics shows the versatility of the theory. For example, while in Li and Be the band structure effects are supposed to be important, in

heavier metals like Rb, Cs and Zn, the spin–orbit effects contribute significantly. The success of this theory clearly shows that various important contributing mechanisms have been taken into account adequately. Finally, we note that the theory is general and can be applied to other metals where the pseudopotential formalism is valid.

## Acknowledgment

## References

Anderson W T Jr, Ruhlig M and Hewitt R 1967 *Phys. Rev.* **161** 293
Ashcroft N W 1968 *J. Phys. C: Solid State Phys.* **1** 232
Barnaal D F, Barnes R G, McCart B R, Mohn L W and Torgeson D R 1967 *Phys. Rev.* **157** 510
Clementi E 1966 *Tables of Atomic Functions* (San Jose: IBM)
Cohen M H, Goodings D A and Heine V 1959 *Proc. Phys. Soc.* **73** 811
Ese D and Reissland J C 1973 *J. Phys. F: Met. Phys.* **3** 2066
Gaspari G D, Shyu W M and Das T P 1964 *Phys. Rev.* **134** A852
Gerstner G and Cutler P H 1969 *Phys. Lett.* **30** 368
Harrison W 1966 *Pseudopotentials in the Theory of Metals* (Massachusetts: Benjamin)
Herman F and Skillman S 1963 *Atomic Structure Calculations* (Englewood Cliffs, NJ: Prentice-Hall) p 90
Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Hubbard J 1957 *Proc. Phys. Soc.* A **240** 539
—— 1958 *Proc. Phys. Soc.* A **283** 336
Jena P, Mahanti S D and Das T P 1968 *Phys. Rev. Lett.* **20** 544
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
Landau L 1930 *Z. Phys.* **64** 629
Mahanti S D and Das T P 1971 *Phys. Rev.* B **3** 1599
Mahanti S D, Tterilikkis L and Das T P 1970 *Magnetic Resonance* ed C K Coogan *et al* (New York: Plenum)
Mann J B 1968 *Atomic Structure Calculations* (Los Alamos: NTIS)
Manninen M and Jena P 1980 *J. Phys. F: Met. Phys.* **10** 1567
Mishra B, Das L K, Sahu T, Tripathi G S and Misra P K 1984 *Phys. Lett.* A **106** 81
Mishra B, Sahu T, Tripathi G S and Misra P K 1986 *Phys. Lett.* A **114** 272
Misra P K, Mohanty S P and Roth L M 1971 *Phys. Rev.* B **4** 1799
Misra P K and Roth L M 1969 *Phys. Rev.* **177** 1089
Nusair M, Wilk L and Vosko S H 1981 *J. Phys. F: Met. Phys.* **11** 1683
Perdew J P and Wilkins J W 1973 *Phys. Rev.* B **7** 2461
Petzinger and Munjal 1977 *Phys. Rev.* B **15** 1560
Phillips J C and Kleinman L 1959 *Phys. Rev.* **123** 420
Sham L J 1955 *Proc. Phys. Soc.* A **283** 33
Shaw R W 1968 *Phys. Rev.* **174** 769
Shaw R W and Harrison W 1967 *Phys. Rev.* **163** 604
Styles G A and Tranfield G 1978 *J. Phys. F: Met. Phys.* **8** 2035·
Townes C H, Herring C and Knight W D 1950 *Phys. Rev.* **77** 852
Tripathi G S 1985 *J. Phys. C: Solid State Phys.* **18** L1157
Tripathi G S, Das L K, Misra P K and Mahanti S D 1981 *Solid State Commun.* **38** 1207
—— 1982 *Phys. Rev.* B **25** 3091
Tripathi G S, Mishra B and Misra P K 1987 *J. Magn. Mater.* **67** 271
Tripathi G S, Misra C M, Tripathi P and Misra P K 1989 *Phys. Rev.* B **39** 94
Tterilikkis L, Mahanti S D and Das T P 1969 *Phys. Rev.* **178** 630
Weisz G 1966 *Phys. Rev.* **149** 504
Wilk L, Nusair M and Vosko S H 1981 *Can. J. Phys.* **59** 585
Zaremba E and Zobin D 1980 *Phys. Rev. Lett.* **44** 175