# A SIMPLE DERIVATION OF THE BLOCH EQUATIONS FOR LOCALIZED MOMENT E.S.R. IN METALS IN THE PRESENCE OF ANISOTROPY

## By D. A. Smith*

### Abstract

A density-matrix approach is used to derive the coupled Bloch equations for the electron spin resonance of localized moments and conduction electrons in metals, including anisotropy fields acting on the local moments. The equations agree with those obtained elsewhere by more sophisticated many-body techniques. In particular, it is demonstrated explicitly that relaxation proceeds towards instantaneous equilibrium.

## I. INTRODUCTION

It is now widely accepted that the phenomenological Bloch equations proposed by Hasegawa (1959) provide a working description of the electron spin resonance of magnetic impurity spins and conduction electrons in metals (a simple discussion and references to experimental work are given by Winter 1971). However, Hasegawa's equations were purely phenomenological and only recently has a complete microscopic derivation been given (Langreth and Wilkins 1972, Barnes and Zitkova 1973). The purpose of the present paper is to provide an alternative derivation which does not require an extensive use of many-body theory.

The influence of anisotropy fields on the local moments leads to considerable modifications in the Bloch equations. These have been charted by S. E. Barnes (to be published), using diagrammatic methods. Barnes's equations, which may also be obtained with the density-matrix methods used here, are applicable to rare-earth impurities in metals and also to 3d impurities in the presence of neighbouring heavy atoms (see Smith and Haberkern 1973 and references therein).

## II. DENSITY-MATRIX DERIVATION

The derivation of the Bloch equations from the equation of motion of the density matrix is moderately straightforward but involves a number of plausible assumptions that are apparently not required in more sophisticated treatments. Thus the density-matrix technique, while less rigorous, may be of value because of the insight it provides into the microscopic content of the Bloch equations.

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Let the total Hamiltonian at time $t$ be written as

$$\mathcal{H}(t) = \mathcal{H}_0(t) + \mathcal{H}_1, \tag{1}$$

where $\mathcal{H}_0(t)$ is the sum of the internal Hamiltonians of the conduction electron and local moment spin systems (usually labelled s and d respectively), including their coupling to magnetic fields, and $\mathcal{H}_1$ is the s–d exchange interaction. The mean field terms should be removed from $\mathcal{H}_1$ to $\mathcal{H}_0$ so that the former has zero thermodynamic average and causes only cross-relaxation between the spin systems. We then follow a well-trodden route to a master equation (e.g. Abragam 1961) and write the equation of motion of the density matrix in an interaction representation which transfers all the time dependence into $\mathcal{H}_1$ as

$$i\, d\rho^*/dt = [\mathcal{H}_1^*(t), \rho^*(t)], \tag{2}$$

where

$$\rho^*(t) = U(t)\rho(t)U^{-1}(t) \tag{3}$$

with a similar definition for $\mathcal{H}_1^*(t)$. Here $\rho(t)$ is the density matrix in the Heisenberg representation. The unitary transform $U(t)$ satisfies the relation

$$dU/dt = i\, U(t)\mathcal{H}_0(t) \qquad \text{with} \qquad U(0) = 1. \tag{4}$$

By integrating equation (2) from times 0 to $t$ and substituting the result into the right-hand side of (2), we have

$$d\rho^*(t)/dt = -i[\mathcal{H}_1^*(t), \rho(0)] - \int_0^t [\mathcal{H}_1^*(t), [\mathcal{H}_1^*(t'), \rho^*(t')]]\, dt'. \tag{5}$$

Equation (5) is so far exact. We shall now assume that:

(i) $\rho(0)$ can be replaced by $\rho^*(t)$ in the first term on the right-hand side of (5) and

(ii) $\rho^*(t')$ can be similarly replaced by $\rho^*(t)$ in the second term on the right-hand side while the lower limit of the integration can be extended to $-\infty$.

Both assumptions are expected to be reasonable when the correlation time $\tau_c$ of the perturbation $\mathcal{H}_1$ is small compared with the time scale of interest, i.e. for $t \gg \tau_c$. More precisely $\tau_c$ is the characteristic time of the fluctuating component of the internal fields and is therefore different for the two spin systems: for the s field $\tau_c \sim h/k_B T$, where $k_B$ is Boltzmann's constant and $T$ the absolute temperature, while for the d field $\tau_c \sim h/\varepsilon_F \approx 10^{-15}$ s, where $\varepsilon_F$ is the Fermi energy of the conduction electrons. In a sense, both spin systems are motionally narrowed; the s spins because of the band motion of the conduction electrons and the d spins because of the high fluctuation rate of their internal fields, which cause transitions between the Zeeman levels.

In the above situation one expects that the magnetizations will relax to their instantaneous equilibrium values, which is the main result of Barnes and Zitkova (1973). Instantaneous equilibrium is described by the density matrix

$$\rho_0(t) = \exp(-\beta \mathcal{H}_0(t))/\text{tr}\{\exp(-\beta \mathcal{H}_0(t))\} \tag{6}$$

with $\beta = 1/k_{\mathrm{B}} T$. This result can be obtained from the identity

$$\int_{-\infty}^{\infty} [\mathscr{H}_1^*(t-\tau), \mathscr{H}_0(t-\tau)]\, \mathrm{d}\tau \equiv -\mathrm{i} \int_{-\infty}^{\infty} \frac{\mathrm{d}\{\mathscr{H}_1^*(t-\tau)\}}{\mathrm{d}\tau}\, \mathrm{d}\tau = 0, \qquad (7)$$

which follows from equations (3) and (4), and the relation

$$\int_{-\infty}^{\infty} [\mathscr{H}_1^*(t-\tau), (\mathscr{H}_0(t-\tau))^n]\, \mathrm{d}\tau = 0, \qquad n \geqslant 1. \qquad (8)$$

This is a generalization of (7) and follows by induction for arbitrary $n$ from the result for $n = 2$ found by expanding the commutator and replacing $t-\tau$ by $t$ in the argument of that factor $\mathscr{H}_0$ which lies outside the inner commutator; this step is merely an application of the assumption (ii) above. Hence we have

$$\int_{-\infty}^{\infty} [\mathscr{H}_1^*(t-\tau), \rho_0(t-\tau)]\, \mathrm{d}\tau = 0 \qquad (9)$$

by assuming an expansion of $\rho_0$ in positive powers of $\mathscr{H}_0$ or traces thereof. The result (9) suffices to show that the second term on the right-hand side of (5) is zero when $\rho^* = \rho_0$, since by putting $t' = t-\tau$ and using the assumption (ii) the $\tau$ integration extends from 0 to $\infty$; this range may be finally changed to $(-\infty, \infty)$ with an extra factor of $\frac{1}{2}$ if imaginary terms are neglected (see equation (16) in Section III below).

By incorporating all the above steps and finally reverting to the Heisenberg representation, we obtain the desired equation of motion

$$\mathrm{d}\rho/\mathrm{d}t = -\mathrm{i}[\mathscr{H}_0(t)+\mathscr{H}_1, \rho(t)]$$

$$- \int_0^\infty [\mathscr{H}_1, [\exp(-\mathrm{i}\mathscr{H}_0\tau)\, \mathscr{H}_1 \exp(\mathrm{i}\mathscr{H}_0\tau), \rho(t)-\rho_0(t)]]\, \mathrm{d}\tau. \qquad (10)$$

A further approximation has been anticipated in the last term by ignoring the time dependence of $\mathscr{H}_0$, which is due to coupling with the r.f. field, and using $U(t) = \exp(\mathrm{i}\mathscr{H}_0 t)$. This is permissible in the weak-field limit (approximation (iv) in Section III below).

Nothing has yet been said about assumption (i) above, which determines the form of the term $-\mathrm{i}[\mathscr{H}_1, \rho(t)]$ in equation (10). The consequences of (i) may be avoided completely by removing the mean field terms from $\mathscr{H}_1$, for this term then gives zero contribution to the Bloch equations.

### III. COUPLED BLOCH EQUATIONS

Equation (10) can now be used to derive the Bloch equations for the total s and d magnetizations. It is instructive to do this in a rotationally invariant form, which is possible in the absence of anisotropy because the s–d exchange interaction is invariant under a joint rotation of s and d spins, i.e. it commutes with the total spin.

The localized spins, denoted by $S_i$, are assumed to be distributed at random over $N$ lattice sites of the crystal with concentration $c$ while the g-factors $g_s$ and $g_d$ of the two spin systems are arbitrary. In an external field $H(t)$ the unperturbed Hamiltonian is

$$\mathscr{H}_0(t) = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} - g_s H_s(t) \cdot \sum_{k\sigma\sigma'} s_{\sigma\sigma'} c_{k\sigma}^+ c_{k\sigma'} - g_d H_d(t) \cdot \sum_i S_i, \qquad (11)$$

comprising the band energy of the conduction electrons and the Zeeman interactions. Here $c_{k\sigma}$ and $c_{k\sigma}^+$ are annihilation and creation operators for an electron in a Bloch state of wave vector $k$ and spin $\sigma = \pm 1$ with energy $\varepsilon_k$, and $s$ is a vector whose components are half the Pauli matrices. The s–d exchange interaction, in a form appropriate for transition-ion impurities (Schrieffer 1967), will be written as

$$\mathscr{H}_1 = -(5J/N) \sum_{ikk'\sigma\sigma'} \exp\{-i(k-k') \cdot R_i\} P_2(\hat{k} \cdot \hat{k}') \delta S_i \cdot s_{\sigma\sigma'} \delta(c_{k\sigma}^+ c_{k'\sigma'}), \qquad (12)$$

where the $R_i$ are the localized spin sites, $P_2$ is a Legendre polynomial of second order, and, for any operator $A$, $\delta A = A - \langle A \rangle$ where $\langle A \rangle$ is the thermodynamic average in the presence of $\mathscr{H}(t)$. These mean field subtractions, which must therefore appear in equation (11), do so in the guise of the effective fields

$$H_d(t) = H(t) + \lambda M_s(t), \qquad H_s(t) = H(t) + \lambda M_d(t), \qquad (13)$$

where $\lambda = 5J/g_s g_d N$ is the Weiss field constant and the instantaneous magnetizations $M_s$ and $M_d$ are given by

$$M_s(t) = g_s \operatorname{tr}\left(\sum_{k\sigma\sigma'} s_{\sigma\sigma'} c_{k\sigma}^+ c_{k\sigma'} \rho(t)\right), \qquad M_d(t) = g_d \operatorname{tr}\left(\sum_i S_i \rho(t)\right). \qquad (14)$$

With the definitions (14), the Bloch equations may be derived from (10). The calculation is helped considerably by using the identities

$$\operatorname{tr}\big(M[\mathscr{H}_0, \rho]\big) \equiv \operatorname{tr}([M, \mathscr{H}_0]\rho), \qquad (15a)$$

$$\operatorname{tr}\big(M[\mathscr{H}_1, [\mathscr{H}_1(-\tau), \rho]]\big) \equiv \operatorname{tr}\big([[M, \mathscr{H}_1], \mathscr{H}_1(-\tau)]\rho\big), \qquad (15b)$$

which remove the need for an explicit representation of the density matrix. The required commutators will not be displayed as they readily follow from the commutation rules for fermion and spin operators. However, the final result requires the additional assumptions:

(iii) $\rho(t) = \rho_d(t)\rho_s(t)$, where $\rho_d$ and $\rho_s$ operate exclusively in the d and s subspaces respectively; this means that s–d correlations are neglected, as is to be expected from what is essentially a mean field theory; and

(iv) $H_d$ and $H_s$ are very much less than $k_B T$ (where we use energy units for magnetic fields so that the Bohr magneton is unity); this weak-field limit is the usual experimental situation.

The assumption (iv) implies that the magnetizations are small and the basic equation (10) may be linearized about equilibrium. In fact this need only be done implicitly.

When evaluating an object like

$$\text{tr}(\mathcal{O}\,\rho) = \text{tr}(\mathcal{O}\,\rho_s\,\rho_d)\,,$$

the contribution which produces a result containing $M_s$ can be evaluated by replacing $\rho_d$ by its high-temperature limit $(2S+1)^{-cN}$, $S$ being the principal quantum number of each local moment. Similarly, the contribution which leads to $M_d$ can be evaluated by using the zero-field approximation to $\rho_s$.

In the relaxation terms there appears the time integral

$$\int_0^\infty \exp\{i(\varepsilon - \varepsilon')\tau\}\,\mathrm{d}\tau = \lim_{\delta \to 0^+} i/(\varepsilon - \varepsilon' + i\delta) \approx \pi\delta(\varepsilon - \varepsilon')\,, \tag{16}$$

if the principal part is neglected. The neglected term should in principle give rise to the "Kondo $g$-shifts" proportional to $\ln T$, but these are beyond the scope of the density-matrix method (see Langreth and Wilkins (1972) for a discussion of this and related matters).

In this way one arrives at the Bloch equations of Barnes and Zitkova (1973) in vector form:

$$\frac{\mathrm{d}M_d}{\mathrm{d}t} = g_d\,M_d \times H_d(t) - \frac{M_d - \chi_d H_d}{T_{ds}} + \frac{g_d}{g_s}\frac{M_s - \chi_s H_s}{T_{sd}}\,, \tag{17a}$$

$$\frac{\mathrm{d}M_s}{\mathrm{d}t} = g_s\,M_s \times H_s(t) - \frac{M_s - \chi_s H_s}{T_{sd}} + \frac{g_s}{g_d}\frac{M_d - \chi_d H_d}{T_{ds}}\,, \tag{17b}$$

where

$$\chi_d = cN g_d^2 S(S+1)/3k_B T\,, \qquad \chi_s = \tfrac{1}{2}g_s^2 N\rho \tag{18}$$

and

$$T_{ds}^{-1} = 5\pi(J\rho)^2 k_B T\,, \qquad T_{sd}^{-1} = \tfrac{10}{3}\pi c J^2 \rho S(S+1)\,. \tag{19}$$

Here $\rho$ is the electronic density of states per atom per one spin direction. The equations (17) are basically those postulated by Hasegawa (1959) but are modified to include $g$-factor ratios in the cross-relaxation terms (Brenig *et al.* 1970) and relaxation to instantaneous equilibrium in the presence of d.c. and r.f. magnetic fields (Barnes and Zitkova 1973). A slight generalization that is desirable to describe transmission e.s.r. experiments is that when the r.f. field is spatially varying a diffusion term

$$D\nabla^2(M_s - \chi_s H_s) \tag{20}$$

should appear in the right-hand side of equation (17b). The diffusion constant $D$ can be frequency-dependent but the low-field and low-frequency limit of $\tfrac{1}{3}v_F^2\tau$, where $v_F$ is the Fermi velocity and $\tau$ the relaxation time appearing in the electrical resistivity, is usually applicable for the dilute alloy systems.

## IV. Effects of Anisotropy

If the localized spins see an anisotropy field then, strictly speaking, it will not be possible to generate Bloch equations in the form of linear differential equations in $M_d$ and $M_s$. This is because the equation of motion for $\langle S_i \rangle$ will involve tensor averages like $\langle S_i S_i \rangle$ of an even number of spin operators for which additional

equations of motion will be required, giving $2S+1$ equations in all. This mode of description leads directly to the use of irreducible tensor operators and will not be considered here. Instead we choose a particular simple geometry for the various fields and confine our attention to verification of the linearized Bloch equations for the transverse r.f. susceptibilities first derived by S. E. Barnes (to be published).

For simplicity consider a uniaxial anisotropy field of the form

$$\mathscr{H}_a = -\sum_i \mathbf{S}_i \cdot \mathbf{F} \cdot \mathbf{S}_i, \tag{21}$$

where the tensor $\mathbf{F}$ is diagonal if the crystal axes are chosen as cartesian coordinate axes. However, the usual experimental situation is that there is a large d.c. magnetic field $H$ at some arbitrary direction with respect to the crystal axes and an arbitrarily small r.f. field $h(t)$ perpendicular to $H$. If we have

$$|\mathbf{F}| \ll H, \tag{22}$$

which is a high-field situation with regard to anisotropy, then the energy levels $E_M$ of a single localized spin are given approximately by first-order perturbation theory as

$$E_M = -Mg_d H - (M|\mathbf{S}\cdot\mathbf{F}\cdot\mathbf{S}|M) \equiv -Mg_d H - FM^2, \qquad -S \leqslant M \leqslant S, \tag{23}$$

where $M$ is an eigenvalue of $S^z$ and the $z$ axis is parallel to $H$. The anisotropy also mixes spin eigenstates $|M\pm 1)$ and $|M\pm 2)$ into the state $|M)$ with weights of the order of $F/H$, producing satellite resonances at frequencies $g_d H \pm (g_d H, 2g_d H)$ with intensities proportional to $(F/H)^2$. Thus the dominant effect is in the energy levels where only the diagonal matrix elements of (21) are required, and for this situation it is sufficient to take

$$\mathscr{H}_a = -F \sum_i (S_i^z)^2. \tag{24}$$

Now let the r.f. field be circularly polarized in the anticlockwise sense about the $z$ axis with frequency $\omega$, so that $h_x(t) = h\cos\omega t$ and $h_y(t) = -h\sin\omega t$. Then the Zeeman interaction with the r.f. field is

$$-\tfrac{1}{2}g_d h \sum_i \{\exp(-i\omega t)S_i^- + \text{h.c.}\} - \tfrac{1}{2}g_s h \sum_k \{\exp(-i\omega t)c_{k\downarrow}^+ c_{k\uparrow} + \text{h.c.}\}, \tag{25}$$

where $S^\pm = S^x \pm iS^y$ as usual. We retain only the first term in each summation and calculate the linear responses

$$M_s^+(t) = \text{tr}\left(g_s \sum_k c_{k\uparrow}^+ c_{k\downarrow}\, \rho(t)\right) = \chi_s^+(\omega)\, h\exp(-i\omega t), \tag{26a}$$

$$M_M^+(t) = \text{tr}\left(g_d \sum_i S_{iM}^+ \rho(t)\right) = \chi_M^+(\omega)\, h\exp(-i\omega t), \tag{26b}$$

where

$$S_{iM}^+ = S_i^+ P_{iM} \qquad \text{with} \qquad P_{iM} = |iM)(iM|, \tag{27}$$

$P_{iM}$ being a projection operator onto the state $|iM)$. Thus equation (26b) gives the

response of those localized spins making transitions from $|M\rangle$ to $|M+1\rangle$, for which the resonance frequency is given by

$$-E_{M+1}+E_M = g_d H + (2M+1)F. \tag{28}$$

This suggests that $M$ can be restricted to the range $(-S, S-1)$, giving $2S+1$ Bloch equations in all.

From here the calculation proceeds as in Section III. Our final results, written in a form as close as possible to (17), are

$$-i\omega M_s^+ = -ig_s(H_s^z M_s^+ - H_s^+ M_s^z) - \frac{M_s^+ - \chi_s H_s^+}{T_{sd}} + \frac{g_s}{g_d}\frac{M_d^+ - \chi_d H_d^+}{T_{ds}}, \tag{29a}$$

$$-i\omega M_M^+ = -ig_d(H_d^z M_M^+ - H_d^+ M_M^z) - i(2M+1)F(M_M^+ - \chi_M H_d^+)$$

$$-\frac{a_M(M_M^+ - \chi_M H_d^+)}{T_{ds}} + \frac{a_M(M_{M+1}^+ - \chi_{M+1} H_d^+)}{2T_{ds}} + \frac{a_M(M_{M-1}^+ - \chi_{M-1} H_d^+)}{2T_{ds}}$$

$$+\frac{g_d}{g_s}\frac{b_M(M_s^+ - \chi_s H_s^+)}{T_{sd}}, \tag{29b}$$

where

$$_M v = S(S+1) - M(M+1), \qquad b_M = 3a_M/2S(S+1)(2S+1). \tag{30}$$

The other parameters are defined, in keeping with equations (26) and (13), as

$$M_s^z = \chi_s(1+\lambda\chi_d)H, \qquad\qquad M_M^z = \chi_M(1+\lambda\chi_s)H, \tag{31}$$

$$H_s^z = H(1+\lambda\chi_d), \qquad\qquad H_d^z = H(1+\lambda\chi_s), \tag{32}$$

$$H_s^+ = h\exp(-i\omega t)(1+\lambda\chi_d^+(\omega)), \qquad H_d^+ = h\exp(-i\omega t)(1+\lambda\chi_s^+(\omega)), \tag{33}$$

with

$$\chi_M = b_M \chi_d. \tag{34}$$

Finally, the definition of $M_M^+$ implies the connecting relation

$$\sum_M M_M^+ = M_d^+ \tag{35}$$

which closes the equations (29). Similar relations also hold for $M_M^z$ and $\chi_M$ since the sum of all the $b_M$'s is unity.

The Bloch equations (29) agree with those obtained by Barnes. They are valid for small anisotropy and high temperatures, i.e. for $F \ll H \ll k_B T$. It should be noted that more complicated forms for the anisotropy can easily be inserted, since these conditions imply that the relaxation rates themselves are not affected by anisotropy. The only place in equations (29) where $F$ appears explicitly is in the bare d resonance frequency.

## V. Concluding Remarks

A proper discussion of the Bloch equations (17) and (29) is out of place here. It is sufficient to state that (17) satisfies several test conditions which are required on very general grounds (Brenig *et al.* 1970) and that the effective fields (13) are defined only to first order in $J$. A complete treatment to $O(J^2)$ would include Kondo $\ln T$ terms in various places, as discussed by Langreth and Wilkins (1972), but these appear to be well-nigh unobservable experimentally. The solution of the linearized version of (17) is well documented (see e.g. Dupraz *et al.* 1970). Approximate solutions to the Barnes equations (29) in various limiting cases have been given by Smith and Haberkern (1973) together with a discussion of the relation between equations (29) and (17).

Finally, spin-lattice relaxation should be included in the Bloch equations for a satisfactory description of experimental results. This subject is adequately reviewed by Winter (1971).

## VI. Acknowledgments

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