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Models for the NMR parameters in systems of small metal particles

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Abstract. In the literature on nuclear magnetic resonance in small metal particles, three main lines of approach are found which lead to qualitatively different predictions for the behaviour of Knight shift and, where available, for the linewidth. In this paper it is shown how these differences arise as consequences of the different sets of starting hypotheses used in each type of approach. Some characteristics of the nuclear spin–lattice relaxation are discussed as well, and attention is given to experimental considerations.

1. Introduction

Until fairly recently, most discussions of NMR data for small metallic particles were given in the context of Kubo's theory of the spin susceptibility of free and independent electrons in a small system [1], later refined in the influential paper by Denton and coworkers [2]. The central assumptions are that the particles that make up a sample are completely isolated from each other (exchange of electrons between them is excluded) and that their one-electron energy level structures are all different (even if they contain the same number of electrons). It is furthermore supposed that the degeneracy of the one-electron energy levels is completely lifted, except Kramers' (or spin) degeneracy (in Kubo's Poisson distribution [3], however, accidental degeneracies are allowed). It turns out that the occupancy (single or double) of the highest occupied level at zero temperature divides the thermal behaviour into two types: that of 'odd' and that of 'even' particles. The particle size distribution in the sample must be taken into account as an additional effect in comparing with the theory: its most perturbing effect will be that the sample may contain both even and odd particles.

Twenty years ago, Yee and Knight [4] studied the NMR of copper particles with mean diameters between 2.5 and 45 nm. They found NMR signals that are considerably broadened with respect to the bulk, that show asymmetric lineshapes with long tails toward low field, and that have absorption maxima that occur to high field (towards lower Knight shift) of the bulk resonance. It is customary to ascribe the low-field tail to signals from odd particles, and to consider the absorption maximum as the maximum of a symmetric resonance line due to even particles. The maximum of a symmetric NMR line coincides with its first moment; the shift of the first moment (with respect to the resonance frequency of a 'bare' nucleus) is linearly related to the electron spin susceptibility. In this interpretation, the shift of the absorption maximum is given by the even-particle susceptibility of Kubo theory. If however one ignores the odd/even distinction when looking at their NMR lines, there is little evidence that the first moment does not coincide with the bulk resonance position: in that case the observation that remains to be explained is the asymmetric lineshape and the temperature

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dependent broadening. These three features are contained in recent theoretical work by Beenakker [5] and by Efetov and Prigodin [6].

For the susceptibility, the latter authors find a temperature-independent, Pauli-like behaviour, and ascribe this to their using the grand canonical ensemble. It is known however [2, 7] that, when the restriction of electron conservation is lifted in the reasoning of Denton *et al* [2], the behaviour of the susceptibility remains qualitatively similar (odd/even effects, temperature dependence) to that found in the canonical ensemble. In fact, this result of Efetov and Prigodin (and a similar conclusion by Beenakker) is due to a fundamental difference between the descriptions of the experimental systems in their work and in Kubo type theories. Since this point has remained somewhat obscure, this paper will start by describing a similar model (the 'tunnelling/localization' model) in some detail, and establish, without referring to random matrix theory (RMT), rather general equations for the susceptibility χ, the Knight shift K, the second moment of the NMR line $\overline{\Delta K^2}$ and the nuclear spin–lattice relaxation T_1^{-1}. Then we make the identifications between variables occurring in our formulation and in RMT, especially to find a connection with Beenakker's results [5] for χ, K and $\overline{\Delta K^2}$, and go on to discuss spin–lattice relaxation. Finally, we make a brief comparison with the 'exponential healing' types of parametrization [8, 9] that have been used to describe experimental NMR spectra of small platinum particles. The original 'isolated particle' model has been repeatedly reviewed [10–12], and here we will only mention its conclusions, concerning χ and K (no results are known for the second moment).

2. The tunnelling/localization model

The experimental sample is considered to consist of N randomly packed metallic particles, separated from each other by tunnel barriers. The packing of the particles is supposed to lack perfect translation symmetry, so that they all have slightly different electronic properties except that each particle has volume v, and contains on average M electrons. At the outset therefore, one considers an $(N \times M)$-electron system, representing a macroscopic piece of material. This is very different from the strictly non-interacting small particle, containing a limited number of electrons, that is the basic object in Kubo type theories. The energy level distribution of the total $(N \times M)$-electron system is (quasi-) continuous, but each of the corresponding eigenfunctions is supposed to be well localized in only one of the N particles. We number the particles with an index α, and the energy levels that have their associated eigenfunctions localized within α with an index k ($k = 0$ is the lowest-energy level localized in α). Due to the tunnelling within the $(N \times M)$-electron system, an electron *can jump out of level* (α, k) *and another into it without strict local conservation of energy*. We assume that the probability distribution of the energy of the electron in level (α, k) is given by a normalized Lorentzian $L(E - E_k^\alpha)$; for simplicity its width $\gamma/2$ is supposed to be independent of (α, k):

$$L(E) = (1/\pi)(\gamma/2)/[E^2 + (\gamma/2)^2]. \tag{1}$$

The charge density distribution of level (α, k), $e|\psi_k^\alpha(r)|^2$, is taken as independent of its energy distribution and therefore as completely specified by the indices α and k. It is normalized within the volume v of particle α, but not necessarily uniform within that volume:

$$|\psi_k^\alpha(r)|^2 = v^{-1} - \varphi_k^\alpha(r) \tag{2a}$$

$$\int_v \varphi_k^\alpha(r)\,\mathrm{d}r = 0. \tag{2b}$$

The functions $\varphi_k^\alpha(r)$ describe the effects of spatial boundary conditions (the spatial distribution of the tunnelling barriers); we neglect the atomic structure and make a jellium type of approximation to describe the electrons within the volume v. An important timescale in NMR of metals is the correlation time for the fluctuations in the contact hyperfine interaction, roughly given by the time it takes for an electron to fly through an atom [13]. If the volume v is sufficiently larger than an atomic volume the average lifetime of the electron in a particle will be much longer than the correlation time, and on the NMR timescale we have a well defined local density of states at energy E at point r of particle α:

$$D^\alpha(E, r) = \sum_k L(E_k^\alpha - E)|\psi_k^\alpha(r)|^2. \tag{3}$$

To calculate thermodynamic properties of the macroscopic sample described above, one proceeds in two steps, as in Kubo theory. In the first step we calculate thermodynamic averages over an ensemble of particles each completely identical to particle α in the sample. These averages are calculated using the Fermi–Dirac distribution function $f(E)$. The total number $(N \times M)$ of electrons in the sample is supposed to be so large, and the temperature so low, that the chemical potential $\mu(N \times M, T)$ of the $(N \times M)$-electron system can be taken as temperature independent: we will call it, as usual, the Fermi energy E_F. Due to the tunnelling contact between the particles, this will also be the chemical potential appearing in the function $f(E)$, independent of the particle index α. In the second average, the differences in level structure E_k^α for different α are taken into account. In our application, this will be done by specifying the correlation functions $R_1(E_1)$ and $R_2(E_1, E_2)$, defined as follows: $R_1(E_1)\,dE_1$ gives that fraction of the N particles that has an energy level in the interval between E_1 and $E_1 + dE_1$ (irrespective of the index k of that level), and $R_2(E_1, E_2)\,dE_1\,dE_2$ gives the fraction that has one level between E_1 and $E_1 + dE_1$, and a second, distinct, level between E_2 and $E_2 + dE_2$.

According to this rule, to obtain the electron spin susceptibility $\overline{\chi}$ of the sample, we calculate first a thermodynamic average for the susceptibility χ^α:

$$\chi^\alpha = -(2\mu_0\mu_B^2/v)\sum_k \int L(E_k^\alpha - E)(\partial f/\partial E)\,dE \tag{4}$$

and next an average over particles α

$$\overline{\chi} = N^{-1}\sum_\alpha \chi^\alpha = -(2\mu_0\mu_B^2/v)\iint R_1(E_1)L(E_1 - E)(\partial f/\partial E)\,dE\,dE_1. \tag{5}$$

To test whether or not all particles in the sample have the same χ, we consider

$$\overline{\Delta\chi^2} = \frac{1}{N}\sum_\alpha(\chi^\alpha - \overline{\chi})^2 \tag{6a}$$

$$\overline{\Delta\chi^2} = (2\mu_0\mu_B^2/v)^2 \iiiint [R_1(E_1)\delta(E_1 - E_2) + R_2(E_1, E_2) - R_1(E_1)R_1(E_2)] \times L(E_1 - E)L(E_2 - E')(\partial f/\partial E)(\partial f/\partial E')\,dE\,dE'\,dE_1\,dE_2. \tag{6b}$$

Similar averages for the Knight shift K are calculated starting from the expression for K at site r in particle α:

$$K(\alpha, r) = -\frac{4}{3}\mu_0\mu_B^2\sum_k |\psi_k^\alpha(r)|^2 \int L(E_k^\alpha - E)(\partial f/\partial E)\,dE. \tag{7}$$

The average over all sites in the volume v of particle α:

$$K^\alpha = v^{-1} \int K(\alpha, r)\,\mathrm{d}v$$
$$= \tfrac{2}{3}\chi^\alpha \tag{8}$$

and the average over all particles α

$$\overline{K} = \tfrac{2}{3}\overline{\chi}. \tag{9}$$

Experimentally, this average Knight shift is given by the position of the first moment (centre of gravity) of the NMR line, not by the position of the maximum amplitude. The second moment of the NMR line is given by

$$\overline{\Delta K^2} = (Nv)^{-1} \sum_\alpha \int (K(\alpha, r) - \overline{K})^2\,\mathrm{d}v$$
$$= (\tfrac{2}{3})^2 \overline{\Delta\chi^2} + (4\mu_0\mu_B^2/3)^2 N^{-1} \sum_\alpha \sum_{kl} A_{kl}^\alpha$$
$$\times \int\int L(E_l^\alpha - E) L(E_k^\alpha - E')(\partial f/\partial E)(\partial f/\partial E')\,\mathrm{d}E\,\mathrm{d}E' \tag{10}$$

with

$$A_{kl}^\alpha = v \int \varphi_k^\alpha(r)\varphi_l^\alpha(r)\,\mathrm{d}v. \tag{11a}$$

Now it is assumed that the $\varphi_k^\alpha(r)$ are such that

$$A_{kl}^\alpha = A_{kk}^\alpha \delta_{kl} \tag{11b}$$

and furthermore that the average, expressed by the sums over α and k in (10), can be taken separately over the A_{kk}^α and the E_k^α:

$$\overline{\Delta K^2} = (\tfrac{2}{3})^2 \overline{\Delta\chi^2} + (4\mu_0\mu_B^2/3)^2 A \int R(E_1) \left[\int L(E_1 - E)(\partial f/\partial E)\,\mathrm{d}E \right]^2 \mathrm{d}E_1. \tag{12}$$

The nuclear spin–lattice relaxation rate T_1^{-1} of a nucleus situated at position r in particle α is given by the Korringa type expression

$$S(T_1(\alpha, r)T)^{-1} = -(4\mu_0\mu_B^2/3)^2 \sum_{kl} |\psi_k^\alpha(r)|^2 |\psi_l^\alpha(r)|^2$$
$$\times \int\int L(E_k^\alpha - E) L(E_l^\alpha - E')(\partial f/\partial E')\delta(E - E' - \hbar\omega)\,\mathrm{d}E\,\mathrm{d}E'. \tag{13}$$

Here S is the Korringa constant, T the temperature and $\omega/2\pi$ the difference between Larmor frequencies of the electron and of the nucleus, and we have used the fact that $f(E)$ varies slowly over an interval $\hbar\omega$. Experimental determinations of spin–lattice relaxation are often performed at a given position in the NMR line, at fixed K. At low temperatures $\partial f/\partial E' = -\delta(E' - E_F)$. If furthermore it is found experimentally that at fixed K the value of T_1 is independent of the field, then one has

$$S(T_1(\alpha, r)T)^{-1} = K^2(\alpha, r). \tag{14}$$

The right-hand side may be temperature dependent, but this equation says that all nuclei that resonate at a given K have the same relaxation time, and therefore the relaxation curves must be exponential, if the conditions of low temperatures and of field independence are fulfilled. It is unlikely that (14) gives a numerically correct value for the relation between T_1 and K, because of susceptibility enhancement effects [14].

3. Results from random matrix theory

In the bulk, the Pauli susceptibility and the Knight shift are independent of the applied field, and they are therefore zero-field properties that can be calculated by perturbation field theory. In the first step of Kubo type theories, exactly such a perturbation theory is applied to a (canonical) ensemble of particles that all have the same one-electron energy level structure; in the second step, one averages over the energy level structures. For consistency, the second step must (like the first one) consider energy level structures in zero applied field. If random matrix theory [15, 16] is used for the second step, the appropriate ensemble is either the orthogonal or the symplectic one: as already remarked by Denton *et al* [2] the unitary ensemble is not suitable to calculate the susceptibility. This can also be seen as follows: consider a neighbouring pair of twofold degenerate levels in a particle belonging to the symplectic ensemble. Switch on a small electric field: each level shows a magnetic splitting, supposed to be small compared to the zero-field splitting between the pair. Increasing the field makes the 'up' level of one member of the pair approach the 'down' level of the other. In the unitary ensemble, crossing of these levels is forbidden, and therefore the incremental susceptibility $\partial M/\partial H$ goes to zero. (However, in Beenakker's calculation [5], the susceptibility is independent of the ensemble used; Efetov and Prigodin [6], who use only the unitary ensemble, find a susceptibility equal to the bulk Pauli value.)

To proceed further with (6) and (12), explicit forms for the correlation functions R_1 and R_2 are needed. It is usual [15] to take

$$R_1(E_1) = \begin{cases} \Delta^{-1} & \text{if } E_1 > 0 \\ 0 & \text{otherwise} \end{cases} \tag{15}$$

with the level spacing Δ independent of E_1 for positive energies. The average number of electrons in a particle is then given by

$$M = 2\Delta^{-1}\int_0^\infty f(E)\,\mathrm{d}E = 2E_F/\Delta. \tag{16}$$

Furthermore, it is supposed that $R_2(E_2, E_1)$ depends on the dimensionless variable $\eta = |E_1 - E_2|/\Delta$ through the two-level cluster function $Y_2(\eta)$:

$$R_2(E_2, E_1) = (1 - Y_2(\eta))R_1(E_1)R_1(E_2). \tag{17}$$

In random matrix theory, the expression for $Y_2(\eta)$ is known [15, 16] for the different ensembles. For the Poisson distribution [3], the energy levels are completely uncorrelated, and therefore $Y_2(\eta) = 0$. It is convenient to introduce the function

$$L_T(E_1) = -\int_{-\infty}^{+\infty} L(E_1 - E)(\partial f/\partial E)\,\mathrm{d}E \tag{18}$$

and to approximate it as the convolution of two Lorentzians:

$$L_T(E_1) \approx (1/\pi)[(\gamma/2) + (4kT/\pi)]/\{(E_1 - E_F)^2 + [(\gamma/2) + (4kT/\pi)]^2\}. \tag{19}$$

As long as $(\gamma/2)+(4kT/\pi)$ is small compared to E_F, integrals over E_1 that involve $L_T(E_1)$ and that, according to (15), should be taken over positive values of E_1 only can be extended from $-\infty$ to $+\infty$, and

$$\int_{-\infty}^{+\infty} L_T(E_1)\,\mathrm{d}E_1 = 1. \tag{20}$$

With equations (5), (9), (18) and (20):

$$\overline{\chi} = \mu_0 \mu_B^2 E_F / v_0 \tag{21a}$$

$$\overline{K} = \tfrac{2}{3}\overline{\chi}. \tag{21b}$$

Here $v_0 = v/M$ is the particle volume per electron, and E_F is the Fermi energy of the system under consideration (metal particles separated by barriers), not necessarily independent of particle size (although later on we will consider this to be the case). Using the approximation (19), and furthermore introducing

$$\alpha = (\gamma + 8kT/\pi)/\Delta \tag{22}$$

(6) can be written as

$$\overline{\Delta\chi^2} = (\pi\alpha)^{-1} g(\alpha) (\overline{\chi})^2. \tag{23}$$

The function $g(\alpha)$ is shown for the different ensembles in figure 1, and explicit forms are given in the appendix. The parameter α describes both size and temperature effects. One may identify the parameter γ with lifetime broadening: $\gamma^{-1} \propto \tau$. The lifetime τ before an electron tunnels out of a particle is supposed to increase with a linear dimension of the particle. The parameter Δ is given by E_F/M; when E_F does not vary with particle size, γ/Δ goes as M/τ, which varies as the surface of the particle. The other contribution to α, $8kT/\pi\Delta$, varies at fixed temperature with the volume of the particle. With the cluster functions of random matrix theory, $\overline{\Delta\chi^2}$ goes to zero for very large α; while for very small values $\overline{\Delta\chi^2}/(\overline{\chi})^2$ increases as α^{-1}. For the Poisson distribution, $g(\alpha) = 1$ for all values of α.

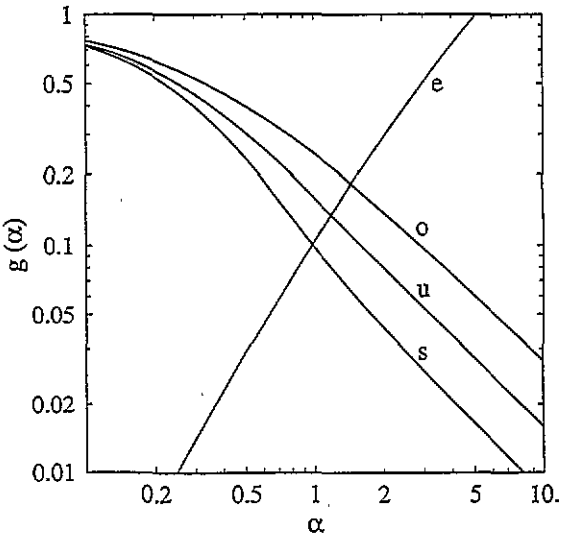

Figure 1. The function $g(\alpha)$ as it appears in (23) and (24) for the symplectic, unitary and orthogonal ensembles (curves labelled s, u, and o) and in (31) for the exponential healing model (curve labelled e). For the Poisson distribution, $g(\alpha) = 1$.

The second moment of the NMR line becomes

$$\overline{\Delta K^2} = (\tfrac{2}{3})^2\overline{\Delta\chi^2} + (\tfrac{2}{3})^2(\pi\alpha)^{-1}(\overline{\chi})^2 A = \overline{K}^2(\pi\alpha)^{-1}(g(\alpha) + A) \tag{24}$$

where the constant A, the particle average of A^{α}_{kk} appearing in (11*b*), has, according to Beenakker [5], the value of two in the orthogonal ensemble, and one-half in the symplectic ensemble. It is unclear what the value of A should be for the Poisson distribution.

The first term in the right-hand side of (24) describes the effect on the NMR frequency of the variation in susceptibility between particles: the stronger the level repulsion, the less variation in χ. The second term describes the site to site variation of the wavefunction within a particle. With the above estimates for A, the wavefunction aspect dominates at high temperature, whereas both effects contribute about equally at low temperature.

The spin–lattice relaxation averaged over all nuclei in the sample is probably not a quantity that is easy to evaluate experimentally, and, as already indicated, the results of free electron theory show only poor agreement with experiments even in the bulk. If nevertheless we calculate the average of (13),

$$\overline{S(T_1T)^{-1}} = \overline{K}^2\left[1 + \frac{\Delta}{2}L(\hbar\omega/2)(1+A) + \frac{\Delta}{2}\int Y_2(\eta)L((\eta\Delta+\hbar\omega)/2)\,\mathrm{d}\eta\right] \tag{25}$$

we find that the right-hand side is temperature independent, so this 'average' relaxation rate should follow the Korringa law $\overline{T_1}T = \text{constant}$.

4. The exponential healing description

The exponential healing description does not consider finite-size effects, and focuses on surface effects instead. The model system is an infinite slab of thickness $2d$. Even for a monolayer, the number of electrons is very large (infinite) and the density of states is continuous. It is supposed that the local density of states at the Fermi level (and therefore the Knight shift) varies with distance x from the centre of the film such that

$$K(x)/K_\infty = 1 - B\exp((|x| - d)/x_0) \tag{26}$$

where the constants B (the fractional reduction of the local density of states in $x = \pm d$), x_0 (the healing length) and K_∞ (the bulk shift) are supposed to be independent of the slab thickness $2d$. The normalized NMR spectrum is given by

$$I(K) = \begin{cases} (x_0/d)(1 - K/K_\infty)^{-1} & \text{for } K_0 < K < K_d \\ 0 & \text{otherwise} \end{cases} \tag{27a}$$

with

$$K_0/K_\infty = 1 - B \tag{27b}$$

and

$$K_d/K_\infty = 1 - B\exp(-d/x_0). \tag{27c}$$

K_0 is the Knight shift at the surface, and K_d that at the centre of the slab. The first moment of the NMR line (and therefore also the susceptibility) of the sample depends on the thickness:

$$\overline{K} = K_\infty - (x_0/d)(\bar{K}_d - K_0). \tag{28}$$

The second moment is given by

$$\overline{\Delta K^2} = (K_\infty - \overline{K})(\overline{K} - \tfrac{1}{2}(K_d + K_0)). \tag{29}$$

In the right-hand side of this equation, the first factor goes to zero for a thick slab, whereas the second factor goes to zero for a thin film. For the spin–lattice relaxation rate, the usual Korringa relation, similar to (14), holds for every position in the NMR line, and the relaxation curves are exponentials. To allow some comparison with the tunnelling/localization model, (24), consider the low-temperature limit of the latter. In this case, α increases as the square of a linear dimension; in the exponential healing description α is replaced by

$$\alpha = (d/x_0)^2 \tag{30}$$

and (29) becomes

$$\overline{\Delta K^2} = (\pi\alpha)^{-1} g(\alpha)(BK_\infty)^2. \tag{31}$$

The function $g(\alpha)$ appearing in this equation is also plotted in figure 1.

The simplicity of the exponential healing approach sketched here (as compared to other treatments [17]) is due to the adoption of the slab geometry, and of course to the lack of sophistication of the approach itself. The calculated variations of the Knight shift in a five-layer (three-site) slab of platinum [18] give some justification for this type of parametrization, but on the other hand, in a free-electron system one expects oscillating, rather than exponential variations in the Fermi level local density of states when going away from the surface [19].

5. Discussion

In recent work on NMR of small copper particles [12] it has been found that the linewidths are not simply proportional to the magnetic field: this indicates that the widths are partially determined by quadrupole interactions, making quantitative comparisons with linewidth theories [5, 6] impossible. On the other hand, the identification of the absorption maximum of these asymmetric NMR lines with the first moment of an even-particle signal [4, 12] rests on the hypothesis that the latter is symmetric.

In platinum catalysts, which consist typically of metal particles with mean diameters between 1.5 and 5 nm, supported on mineral oxides, and separated from each other by distances a few times their diameter, the experimental NMR data from several laboratories [8, 9], typically obtained between 20 K and 200 K can be well described with the exponential healing method: specifically the spectra are temperature independent, and the spin–lattice relaxation time at fixed position in the spectrum obeys T_1T = constant. It is not really understood why platinum particles of this size behave more like macroscopic samples with a large surface/volume ratio than as isolated particle systems; on the other hand, Yee and

Knight have already pointed out [4] that little is known about the validity of the constant-electron-number hypothesis for real samples of metal particles interacting, even weakly, with an embedding matrix.

Some recent work in platinum cluster compounds indicates that towards lower temperatures the relaxation time in this material no longer follows the relation T_1T = constant [20], which has been considered as the hallmark of macroscopic behaviour. The molecules of such compounds consist of a transition metal fragment (up to several hundred atoms) surrounded by a large number of ligands. The samples consist of packed powders containing only these molecules. Since the ligand shells are not very thick compared to the dimension of the metal fragment, such samples behave as semiconductors under an electric field [21], and could be expected to be realizations of the tunnelling/localization model, but, so far, the strong variation of lineshape with temperature expected in the mesoscopic regime [5, 6] has not been observed.

Comparing the predictions from the 'isolated particle', the 'tunnelling/localization' and the 'exponential healing' models for NMR of systems containing small metallic particles, one sees how they are related to the hypotheses underlying the models. The 'isolated particle' model leads to odd/even behaviour for kT smaller than the average level spacing. This occurs even in the grand canonical ensemble, where it is related to temperature variations of the chemical potential, needed to keep the average number of electrons constant when a small, but non-zero, number of energy levels can be attained through thermal excitation. The NMR parameter that has been mainly discussed in this model is $\overline{K}$. It has been remarked that the discreteness of the energy levels should result in extremely long values for the spin–lattice relaxation time [22]. The two other models do not show odd/even behaviour because they start by considering a large system with spatially non-uniform NMR behaviour.

The exponential healing description considers boundary effects in a semi-infinite system. Two parameters are introduced in a rather *ad hoc* fashion: the local susceptibility at the surface (taken as independent of sample thickness) and a characteristic distance over which the susceptibility 'heals back' to its bulk value. Since both parameters are supposed to be independent of temperature, and since the densities of state are continuous and without structure, this parametrization does not 'predict' temperature dependent effects. In the tunnelling/localization model, one finds features of each of the two preceding ones. The densities of state are continuous, and therefore the spin–lattice relaxation curves should be exponential, and the average spin–lattice relaxation time obeys $\overline{T}_1T$ = constant. Since the average density of states at the Fermi level is governed by bulklike behaviour, the average $\overline{K}$ and $\overline{\chi}$ are also independent of temperature. However, there can be considerable structure in the density of states, and this structure may be different from particle to particle. Therefore, the variation in susceptibility when going from particle to particle, expressed by $\overline{\Delta\chi^2}$, is non-zero at low temperature. The second moment of the NMR line, $\overline{\Delta K^2}$, has a contribution due to $\overline{\Delta\chi^2}$, and another due to non-uniformity of the wavefunctions within the particle. The RMT result for the latter contribution [5] is size independent, in sharp contrast to the broadening given in (29), due to a similar phenomenon in the exponential healing description.

The most marked feature that the tunnelling/localization model shares with the isolated particle model is the prediction of temperature dependent effects when $kT \ll E_F/M$ (M is the average number of electrons per particle). Here however, it is $\overline{\Delta K^2}$ that should vary with temperature, while $\overline{K}$ remains constant. Since all $K > 0$, this means that the NMR absorption line is asymmetrical and that its maximum will shift with increasing temperature towards the value of the bulk K. Experimentally, this may be difficult to distinguish from a similar shift of $\overline{K}$ predicted in the isolated particle model (for 'even' particles), unless

the signal to noise ratio is sufficient to allow a clear differentiation between the temperature variations of $\overline{K}$ and of the maximum of the line.

Acknowledgments

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Appendix. Forms of $g(\alpha)$

Starting from (6*b*), (15), (17) and (22), and introducing the auxiliary function

$$L_n(\zeta) = (1/\pi)(\zeta^2 + 1)^{-1} \tag{A1}$$

we find for $g(\alpha)$ appearing in (23)

$$g(\alpha) = 1 - \pi \int_{-\infty}^{+\infty} Y_2(\zeta) L_n(\zeta/\alpha)\, \mathrm{d}\zeta. \tag{A2}$$

For calculations it is easier to work with the two-level form factor $b(k) = b(-k)$:

$$b(k) = \int_{-\infty}^{+\infty} Y_2(r) \exp(2\pi i k r)\, \mathrm{d}r \tag{A3}$$

and to set $a = 2\pi\alpha$. Explicitly forms for the $b(k)$ of the unitary, orthogonal and symplectic ensembles are known. (A2) becomes

$$1 - g(a/2\pi) = a \int_0^{\infty} b(k) \exp(-ak)\, \mathrm{d}k. \tag{A4}$$

A.1. Unitary ensemble

$$b(k) = \begin{cases} 1 - k & \text{for } 0 \leqslant k \leqslant 1 \\ 0 & \text{for } k > 1 \end{cases} \tag{A5}$$

$$g(a/2\pi) = (1 - \exp(-a))/a. \tag{A6}$$

As explained in the text, the unitary results are not relevant to Knight shift measurements; (A6) is given for completeness' sake.

A.2. Orthogonal ensemble

$$b(k) = \begin{cases} 1 - 2k + k \ln(2k + 1) & \text{for } 0 \leqslant k \leqslant 1 \\ -1 + k \ln(2k + 1) - k \ln(2k - 1) & \text{for } k > 1 \end{cases} \tag{A7}$$

$$g(a/2\pi) = (1 - \exp(-a))/a + [-\cosh(a/2) + 2\sinh(a/2)/a]\mathrm{Ei}(-a/2). \tag{A8}$$

A.3. Symplectic ensemble

$$b(k) = \begin{cases} 1 - k/2 + (k/4)\ln|1-k| & \text{for } 0 \leqslant k \leqslant 2 \\ 0 & \text{for } k > 2 \end{cases} \tag{A9}$$

$$g(a/2\pi) = (1 - \exp(-2a))/(4a) + (a+1)\exp(-a)\mathrm{Shi}(a)/(2a). \tag{A10}$$

The symbol $\mathrm{Ei}(x)$ stands for the exponential integral

$$\mathrm{Ei}(x) = -\int_{-x}^{\infty} \frac{\exp(-t)}{t}\,\mathrm{d}t$$

where the principal value of the integral is taken, and

$$\mathrm{Shi}(x) = (\mathrm{Ei}(x) - \mathrm{Ei}(-x))/2.$$

References

[1] Kubo R 1962 *J. Phys. Soc. Japan* **17** 976
[2] Denton R, Mühlschlegel B and Scalapino D J 1973 *Phys. Rev.* B **7** 3589
[3] Kubo R, Kawabata A and Kobayashi S 1984 *Ann. Rev. Mater. Sci.* **14** 49
[4] Yee P and Knight W D 1975 *Phys. Rev.* **11** 3261
[5] Beenakker C W J 1994 *Phys. Rev.* B **50** 15 170
[6] Efetov K B and Prigodin V N 1993 *Phys. Rev. Lett.* **70** 1315
[7] Bucher J P and van der Klink J J 1988 *Helv. Phys. Acta* **61** 760
[8] Makowka C D, Slichter C P and Sinfelt J H 1985 *Phys. Rev.* B **31** 5663
[9] Bucher J P, Buttet J, van der Klink J J and Graetzel M 1989 *Surf. Sci.* **214** 347
[10] Perenboom J A A J, Wyder P and Meier F 1981 *Phys. Rep.* **78** 173
[11] Halperin W P 1986 *Rev. Mod. Phys.* **58** 553
[12] Williams M J, Edwards P P and Tunstall D P 1991 *Discuss. Faraday Soc.* **92** 199
[13] Abragam A 1961 *Principles of Nuclear Magnetism* (Oxford: Oxford University Press) ch IX
[14] Moriya T 1963 *J. Phys. Soc. Japan* **18** 516
[15] Mehta M L 1991 *Random Matrices* (New York: Academic)
[16] Brody T A, Flores J, French J B, Mello P A, Pandey A and Wong S S M 1981 *Rev. Mod. Phys.* **53** 385
[17] van Leeuwen D, van Ruitenbeek J M, Schmid G and de Jongh L J 1992 *Phys. Lett.* **170A** 325
[18] Weinert M and Freeman A J 1983 *Phys. Rev.* B **28** 6262
[19] Kautz R L and Schwartz B B 1976 *Phys. Rev.* B **14** 2017
[20] van der Putten D, Brom H B, Witteveen J, de Jongh L J and Schmid G 1993 *Z. Phys.* D **26** S21
[21] van Staveren M P J, Brom H B and de Jongh L J 1991 *Phys. Rep.* **208** 1
[22] Goto T, Komori F and Kobayashi S 1989 *Z. Phys.* D **12** 415