A Green functions approach to the orientational behaviour of pairs of coupled two-level

tunnelling units

A Green functions approach to the orientational behaviour of pairs of coupled two-level tunnelling units

T Kranjc

Department of Physics, University of Ljubljana, Jadranska 19, 61000 Ljubljana, Slovenia

Abstract. The equation of motion method for the Green functions is applied to study the behaviour of pairs of interacting two-level tunnelling units, coupled with a phonon field to calculate, within the framework of the small-polaron theory, the dynamic susceptibilities and relaxation rates of the system. Explicit expressions for these quantities are obtained in the Debye approximation.

1. Introduction

In recent years intense study, both theoretical and experimental, of glasses and glassy materials has been carried out (Anderson *et al* 1972, Phillips 1972, Hunklinger and Raychaudhuri 1986, for reviews see Phillips 1981). By means of the two-level system (or the tunnelling centre) model the main anomalous low-temperature properties of these materials, such as the linear temperature dependence and the logarithmic time dependence of the specific heat and the T^2 dependence of the thermal conductivity, was successfully explained. However one of the major problems—that concerning the microscopic structure of the tunnelling units and the universality regarding their density of states and their coupling to phonons—has as yet remained unresolved. The question about the nature of the tunnelling states, however, does not arise in the so-called glassy crystals or orientational glasses (Klein 1984, Sethna and Chow 1985). These are crystalline solids containing certain impurities capable of a tunnelling motion which give rise to similar anomalous low-temperature behaviour as—as yet unidentified—two-level tunnelling units in amorphous materials. Examples of such tunnelling centres are the ions OH^-, CN^-, NO_2^-, etc. dissolved in alkali host lattices. The dynamics of the dilute systems of many tunnelling centres (in which case the centres may be considered as isolated units) and their influence on thermal and dielectric properties of doped crystals are well understood (for reviews see Narayanamurti and Pohl 1970, Bridges 1975). At higher concentrations of tunnelling centres, the glassy behaviour sets in, similar to that of other amorphous materials. Whereas in amorphous solids the broad distribution of energy spectrum originates in a distribution of tunnelling parameters and/or asymmetries of the ensemble of the (non-interacting) tunnelling units, it seems that in orientational glasses the broad distribution results from a distribution of interactions between tunnelling units.

   The successful explanation of the low-temperature properties of glassy materials is based essentially on the mean field theory. In the case of amorphous solids, the mean field to which a chosen two-level system (TLS) is coupled is set up by the random

surroundings, creating a distribution in tunnelling and/or asymmetry parameters of double-well potentials in which TLS are confined, while in case of orientational glasses the mean field is built up by the positional and orientational disorder of (identical) tunnelling centres which leads to a distribution in coupling constants.

In some cases, pairs of coupled centres seem to determine certain macroscopic properties; measuring the dielectric constant of several alkali halide crystals doped with paraelectric and paraelastic OH⁻-centres, Potter and Anderson (1981) have observed discrete features which were attributed to reorientational processes of pairs of coupled centres (Moy *et al* 1983, Kranjc 1990). It is the aim of the present paper to develop a low-temperature dynamics of pairs of coupled two-level tunnelling centres (which may be viewed as prototypes of structural units in both the amorphous solids and in orientational glasses), starting from the properties of isolated centres.

In section 2 the model Hamiltonian for the problem is presented. Treating the case of strong coupling between TLS and the crystal lattice, the canonical transformation to displaced lattice oscillators is applied whence the Debye–Waller screening of the tunnelling frequency results, and then linearization with respect to the phonon operators is performed. In section 3, the Green functions and the corresponding dynamical susceptibilities are introduced, and in section 4 the Green functions and relaxation rates for a pair of coupled TLS are calculated. Section 5 gives some concluding remarks.

2. Hamiltonian of a cluster of TLS

A cluster of TLS will be described by a Hamiltonian that is a simple generalization of the one-TLS spin-boson Hamiltonian to which a term describing the interaction between pairs of TLS is included. In the representation of localized states, which are taken to form a complete basis for the TLS space, the Hamiltonian may be written ($\hbar = 1$)

$$\bar{H} = -\sum_k (U_k \sigma_k^z + \Delta_{0k} \sigma_k^x + \mathcal{H}_k \sigma_k^z) + H_L - \sum_{k<l} U_{kl} \sigma_k^z \sigma_l^z$$

$$\mathcal{H}_k = \sum_\lambda \omega_\lambda (\gamma_{k\lambda} a_\lambda^+ + \gamma_{k\lambda}^* a_\lambda) \qquad (1)$$

$$H_L = \sum_\lambda \omega_\lambda a_\lambda^+ a_\lambda.$$

Pauli spin-$\frac{1}{2}$ matrices have been used, Δ_{0k} is the bare matrix element for tunnelling of the kth TLS between the two localized states with asymmetry parameter $2U_k$, and U_{kl} is the interaction energy between the kth and the lth TLS. The term $\mathcal{H}_k \sigma_k^z$ describes the coupling of the kth TLS with the phonon field, a_λ and a_λ^+ being destruction and creation operators, respectively, for a phonon in the mode λ with frequency ω_λ, and $\gamma_{k\lambda}$ and TLS-lattice coupling constants. As usual, the interaction between the TLS and the lattice is taken to be linear in lattice displacements and site-diagonal. Also, only the lowest multiplet of TLS states is taken into account in Hamiltonian (1); such a 'truncated' Hamiltonian (Sethna 1981) is appropriate if the energy of excited TLS states is sufficiently high so that the probability of their being occupied is negligible.

For strong coupling of TLS with the lattice it is convenient to make a unitary transformation

$$H = e^{-S} \bar{H} e^S$$

$$S = \sum_k \hat{A}_k \sigma_k^z \qquad \hat{A}_k = \sum_\lambda (\gamma_{k\lambda} a_\lambda^+ - \gamma_{k\lambda}^* a_\lambda) \qquad (2)$$

which yields

$$H = -\sum_k U_k \sigma_k^z - \sum_k \Delta_{0k}[\sigma_k^x \cosh(2\hat{A}_k) - i\sigma_k^y \sinh(2\hat{A}_k)] + H_L - \sum_{k<l} J_{kl}\sigma_k^z\sigma_l^z + E_b \qquad (3)$$

J_{kl} is the dressed interaction of the TLS in a pair and is given by

$$J_{kl} = U_{kl} + \sum_\lambda \omega_\lambda(\gamma_{k\lambda}\gamma_{l\lambda}^* + \gamma_{k\lambda}^*\gamma_{l\lambda}) \qquad \text{for } k \neq l. \qquad (4)$$

(the second term is the elastic energy) and $J_{kk} = 0$; $E_b = -\sum_{l\lambda} \omega_\lambda |\gamma_{l\lambda}|^2$ is the small-polaron binding energy. As at low temperatures few phonons are excited, we linearize the multiphoton exponential operators in the second term of the Hamiltonian (3) using the Bloch–DeDominicis theorem (see e.g. Nakajima *et al* 1980); retaining only linear terms in a_λ and a_λ^+ gives

$$\cosh(2\hat{A}_k) \simeq \langle\cosh(2\hat{A}_k)\rangle_L = \exp(-W_k) \qquad (5a)$$

$$\sinh(2\hat{A}_k) \simeq 2\hat{A}_k \exp(-W_k) \qquad (5b)$$

where $\langle\ldots\rangle_L$ is the thermal average over the phonon field, and $\exp(-W_k)$ the Debye–Waller factor

$$W_k = 2\sum_\lambda |\gamma_{k\lambda}|^2(2\bar{n}_\lambda + 1) \qquad \bar{n}_\lambda = [\exp(\omega_\lambda/k_B T) - 1]^{-1}$$

k_B is the Boltzmann constant and T the temperature. With the approximation (5), we arrive at an effective Hamiltonian

$$H = -\sum_k U_k \sigma_k^z - \sum_k \Delta_k \sigma_k^x + 2i\sum_k \Delta_k \hat{A}_k \sigma_k^y + H_L - \sum_{k<l} J_{kl}\sigma_k^z\sigma_l^z \qquad (6)$$

from which we have dropped the constant term E_b. The important difference between (1) and (6) is that in (6) renormalized matrix elements $\Delta_k = \Delta_{0k} \exp(-W_k)$ and renormalized interactions J_{kl} appear, an effect which can only be obtained if the interaction between TLS and the lattice is taken into account in all orders in perturbation theory. The Hamiltonian (6) is the same as that obtained by Junker and Wagner (1981) by applying to (3) the Bogoliubov inequality

$$F \leq F_{\text{test}} + \langle H - H_{\text{test}}\rangle^{(\text{test})}$$

H_{test} and F_{test} being the appropriately chosen test Hamiltonian and the corresponding free energy, and retaining, in the variational procedure, only linear terms in phonon operators.

We are interested in the linear response of the system—a cluster of TLS, described by the Hamiltonian (6)—to an external perturbation which we take to be of the form

$$H'(t) = -\sum_k V_k(t)\sigma_k^z. \qquad (7)$$

Such a perturbation describes, for example, a coupling to an external electric field. We assume the perturbation to be switched on adiabatically at $t = -\infty$ and switched off abruptly at time $t = 0$, observing the relaxation of the system towards equilibrium for times $t > 0$; specifically, this means that the time dependence of $V_k(t)$ in (7) is

$$V_k(t) = V_k\theta(-t)\,e^{\varepsilon t}$$

$\theta(t)$ is the step function and $\varepsilon \to 0^+$. From the linear response theory it follows that the time evolution of the deviation of the statistical–mechanical average of σ_k^α, $\alpha = x, y, z$, from its thermal equilibrium value, $\delta\langle\sigma_k^\alpha\rangle(t) = \langle\sigma_k^\alpha\rangle(t) - \langle\sigma_k^\alpha\rangle$, may be written as (see, for example, Nakajima *et al* 1980, p 107, Zubarev 1960)

$$\delta\langle\sigma_k^\alpha\rangle(t) = (i/2\pi)\sum_l V_l \int_{-\infty}^{\infty} \frac{d\omega\, e^{-i\omega t}}{\omega - i\eta}[G_{kl}^{\alpha z}(\omega + i\eta) - G_{kl}^{\alpha z}(\omega - i\eta)] \qquad (8)$$

for $t > 0$ ($\eta \to 0^+$), where.

$$G_{kl}^{\alpha\beta}(t - t') = -i\vartheta(t - t')\langle[\sigma_k^\alpha(t), \sigma_l^\beta(t')]\rangle \qquad (9)$$

are retarded Green functions ($\beta = x, y, z$), and

$$G_{kl}^{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} G_{kl}^{\alpha\beta}(t) \qquad (10)$$

their Fourier transforms. Also in (9) $\sigma_k^\alpha(t)$, etc are operators in the Heisenberg representation

$$\sigma_k^\alpha(t) = \exp(iHt)\sigma_k^\alpha \exp(-iHt)$$

with H given by equation (6).

3. Generalized susceptibilities and relaxation rates

Our aim is to calculate the generalized susceptibilities

$$\chi_{kl}^{\alpha\beta}(\omega) = -2\pi G_{kl}^{\alpha\beta}(\omega) \qquad (11)$$

and relaxation rates which characterize the decay of $\delta\langle\sigma_k^\alpha\rangle(t)$ towards zero. Let us denote

$$G_{kl}^{\alpha\beta}(\omega) \equiv \langle\langle\sigma_k^\alpha; \sigma_l^\beta\rangle\rangle_\omega.$$

The equation of motion for $G_{kl}^{\alpha\beta}(\omega)$ can then be written as

$$\omega\langle\langle\sigma_k^\alpha; \sigma_l^\beta\rangle\rangle_\omega = \langle[\sigma_k^\alpha, \sigma_l^\beta]\rangle + \langle\langle[\sigma_k^\alpha, H]; \sigma_l^\beta\rangle\rangle_\omega. \qquad (12)$$

An appropriate decoupling scheme to truncate the generation of higher-order Green functions will be necessary in solving equation (12).

The case of an isolated TLS has been treated by Junker and Wagner (1981). They calculated $\delta\langle\sigma^z\rangle(t)$ which describes the relaxation behaviour of the system after switching off the external field. We now proceed to the study of the more complex case of two coupled two-level centres.

4. Relaxation of two interacting TLS

The Hamiltonian for two TLS coupled with one another and with the crystal lattice is by (6) equal to

$$H = -\Delta(\sigma_1^x + \sigma_2^x) + 2i\Delta(\hat{A}_1\sigma_1^y + \hat{A}_2\sigma_2^y) + H_L - J\sigma_1^z\sigma_2^z. \qquad (6')$$

We have set $\Delta_1 = \Delta_2 = \Delta$ and $U_1 = U_2 = 0$ which is appropriate for a system of identical TLS with zero asymmetry parameter, as is the case of unbiased orientational glasses.

The configurational space of the Green functions involving only TLS- (called henceforth also spin-) coordinates, which for one TLS has dimension 3, has dimension 15 for two interacting TLS. We exploit the symmetry and choose the basis functions to be

$$G_{KL}(\omega) = \langle\!\langle S_K ; S_L \rangle\!\rangle_\omega \tag{13}$$

where S_K and S_L mean symmetrized combinations of the spin operators, which we take to be the following, for $K = 1$ to 15:

$$
\begin{array}{llll}
(\sigma_1^y + \sigma_2^y)/\sqrt{2} & (\sigma_1^z + \sigma_2^z)/\sqrt{2} & (\sigma_1^x\sigma_2^z + \sigma_1^z\sigma_2^x)/\sqrt{2} & (\sigma_1^x\sigma_2^y + \sigma_1^y\sigma_2^x)/\sqrt{2} \\[2mm]
(\sigma_1^y - \sigma_2^y)/\sqrt{2} & (\sigma_1^z - \sigma_2^z)/\sqrt{2} & (\sigma_1^x\sigma_2^z - \sigma_1^z\sigma_2^x)/\sqrt{2} & (\sigma_1^x\sigma_2^y - \sigma_1^y\sigma_2^x)/\sqrt{2} \\[2mm]
(\sigma_1^x - \sigma_2^x)/\sqrt{2} & (\sigma_1^y\sigma_2^z - \sigma_1^z\sigma_2^y)/\sqrt{2} & (\sigma_1^x + \sigma_2^x)/\sqrt{2} & \\[2mm]
(\sigma_1^y\sigma_2^z + \sigma_1^z\sigma_2^y)/\sqrt{2} & (\sigma_1^z\sigma_2^z - \sigma_1^y\sigma_2^y)/\sqrt{2} & (\sigma_1^z\sigma_2^z + \sigma_1^y\sigma_2^y)/\sqrt{2} & \sigma_1^x\sigma_2^x.
\end{array} \tag{14}
$$

The choice of these symmetry-adapted coordinates leads to splitting of the spin configuration space, under the action of the equation-of-motion operations, into smaller invariant subspaces.

The equation of motion for the function $G_{KL}(\omega)$ is derived in appendix A. In the derivation, the ordinary Tyablikov decoupling scheme has been applied to the higher-order Green functions (see e.g. Parry and Turner 1969)

$$\langle\!\langle AB; C \rangle\!\rangle \approx \langle A \rangle \langle\!\langle B; C \rangle\!\rangle + \langle B \rangle \langle\!\langle A; C \rangle\!\rangle \tag{15}$$

which we consider to be valid if fluctuations of the operator that is replaced by its average value are sufficiently small. This yields the following equation for $G_{KL}(\omega)$:

$$\left[\omega - \mathbf{M} - \sum_{j=1}^{2} \mathbf{B}^j(\omega) \right] \mathbf{G}(\omega) = \mathbf{K} \tag{16}$$

where the elements of the matrix $\mathbf{G}(\omega)$ are $G_{KL}(\omega)$ and the matrices $\mathbf{M}$ and $\mathbf{B}^j$ are given in appendix A.

Two limits may be treated immediately:

(i) Two TLS, coupled to one another, in a static lattice potential ($\gamma_\lambda = 0$). In this case, one obtains from equations (16) and (A.8)

$$
\begin{aligned}
G_{22}(\omega) &\equiv \tfrac{1}{2}\langle\!\langle \sigma_1^z + \sigma_2^z ; \sigma_1^z + \sigma_2^z \rangle\!\rangle_\omega \\
&= -4\Delta[(\omega^2 - 4\Delta^2)\langle\sigma^x\rangle + 4\Delta J \langle\sigma_1^x\sigma_2^x - \sigma_1^y\sigma_2^y\rangle][(\omega^2 - E_+^2)(\omega^2 - E_-^2)]^{-1} \tag{17}
\end{aligned}
$$

where we have taken $\langle\sigma_1^x\rangle = \langle\sigma_2^x\rangle = \langle\sigma^x\rangle$ and $\langle\sigma_1^y\sigma_2^z\rangle = \langle\sigma_1^z\sigma_2^y\rangle = 0$. Further, we have written $E_\pm = E \pm J$. From the excitation spectrum given by the poles of $G_{22}(\omega)$ as $\omega = \pm E_+, \pm E_-$, we may also deduce the energy spectrum of a pair of TLS to be $\omega = \pm E, \pm J$. The average value $\langle\sigma_1^z + \sigma_2^z\rangle$ undergoes an undamped oscillatory motion. From equations (8) and (17) we find

$$
\begin{aligned}
\delta\langle\sigma_1^z + \sigma_2^z\rangle(t) \\
&= (V\Delta/EJ)[(\langle\sigma^x\rangle + D/E_+^2) \cos(E_+ t) - (\langle\sigma^x\rangle + D/E_-^2) \cos(E_- t)] \\
&= (V/\Delta J)[(J/k_B T) \cos(2\Delta^2 t/J) + (\Delta/J)^2 \cos(2Jt)] \tag{18}
\end{aligned}
$$

$$D = -4\Delta[\Delta\langle\sigma^x\rangle + J\langle\sigma_1^x\sigma_2^x - \sigma_1^y\sigma_2^y\rangle].$$

In the last expression in (18), the average values of the spin operators were taken with respect to the Hamiltonian (6') without the spin-lattice coupling term

$$H_0 = -\Delta(\sigma_1^x + \sigma_2^x) + H_L - J\sigma_1^z\sigma_2^z$$

and for $\Delta \ll J$, $J/k_B T \gg 1$ and $\Delta/k_B T \leq 1$.

(ii) In the case of non-interacting TLS ($J = 0$), equations (16) and (A.7), together with equation (8) yield, for example,

$$G_{11} = G_{yy} = G_{22} = G_{zz} = 4\Delta\langle\sigma^x\rangle\{\omega^2[1 - (4\Delta)^2 A(\omega)] - 4\Delta^2\}^{-1}$$

$$A(\omega) = \sum_\lambda \frac{|\gamma_\lambda|^2(2\bar{n}_\lambda + 1)}{\omega^2 - \omega_\lambda^2} \tag{19}$$

which agrees with the calculation by Junker and Wagner (1981). Therefrom the damping constant, i.e. the inverse of the relaxation time for the reorientation of an isolated TLS, may be deduced. In the Debye approximation it is found to be (allowing for the possibility of $U \neq 0$)

$$W = (\Delta^2 P_0/\pi)E' \coth(E'/k_B T)$$

where P_0 is given in (25a) below and $E' = \sqrt{\Delta^2 + U^2}$.

In the following, we consider a pair of TLS, both coupled among themselves and with the lattice vibrations, for the case $\Delta \ll J$. Retaining terms up to the second order in Δ, we arrive, after some calculation, at the following expression for $G_{22}(\omega)$:

$$G_{22}(\omega) = 4\Delta\{\Delta^2\langle\sigma^x\rangle - 2\Delta[2J + (\omega^2 - 4J^2)C_3(\omega)]\langle\sigma_1^x\sigma_2^x - \sigma_1^y\sigma_2^y\rangle\}/D(\omega) \tag{20}$$

where again we have taken $\langle\sigma_1^y\sigma_2^z\rangle = \langle\sigma_1^z\sigma_2^y\rangle = 0$, and $D(\omega)$ is the determinant of the matrix $C^+(\omega)$, equal to

$$D(\omega) = [(\omega - 2\Delta^2 C_4(\omega))^2 - E_+^2][(\omega - 4\Delta^2 C_6(\omega))^2 - (E_- - 4\Delta^2 C_3(\omega))^2]. \tag{21}$$

From $D(\omega)$, we wish to extract the damping constant—the inverse relaxation time—in the motion of a pair of coupled TLS. For $\Delta \ll J$, the poles of $D(\omega)$ are at

$$\omega = \pm 2J \pm (2\Delta^2/J)[1 \pm JC_4(\omega)] \tag{22a}$$

$$\omega = \pm 2\Delta^2/J + 4\Delta^2[C_6(\omega) \mp C_3(\omega)] \tag{22b}$$

with

$$C_4(\omega) = 4 \int J_+(z)(\omega - z)^{-1} \coth(z/2k_B T)\, dz$$

$$C_3(\omega) = -\int J_1(z)\left(\frac{1}{\omega - z - 2J} - \frac{1}{\omega - z + 2J}\right) \coth(z/2k_B T)\, dz \tag{23}$$

$$C_6(\omega) = \int J_0(z)\left(\frac{1}{\omega - z - 2J} + \frac{1}{\omega - z + 2J}\right) \coth(z/2k_B T)\, dz$$

where use has been made of the following spectral functions:

$$J_0(z) = \sum_\lambda |\gamma_\lambda|^2[\delta(z - \omega_\lambda) - \delta(z + \omega_\lambda)]$$

$$J_1(z) = \sum_\lambda |\gamma_\lambda|^2 \cos(\boldsymbol{q}_\lambda \cdot \boldsymbol{R})[\delta(z - \omega_\lambda) - \delta(z + \omega_\lambda)] \tag{24}$$

$$J_\pm(z) = J_0(z) \pm J_1(z).$$

Up to now, no assumption has been made about the nature of the coupling of the TLS with the crystal lattice, except that it is linear in lattice displacements. We now assume the TLS to be coupled to the long wavelength acoustic mode phonons, in which case the deformation potential approximation for the spin-lattice coupling constants may be used, with $\gamma_\lambda \propto 1/\sqrt{\omega_\lambda}$. Furthermore, we take the Debye approximation for the lattice vibrations. The spectral functions $J_\pm(z)$ can then be easily calculated and are found to be

$$J_\pm(z) = (z/8\pi^2)[P_0 \pm P_z(R)] \tag{25}$$

$$P_0 = 4 \sum_{p=1}^{3} v_p^{-3} \langle V'\omega_\lambda|\gamma_\lambda|^2 \rangle_q = 6/(k_B T_0)^2 \tag{25a}$$

$$P_z(R) = \sum_{p=1}^{3} v_p^{-3} \langle V'\omega_\lambda|\gamma_\lambda|^2 \cos(\boldsymbol{q}_\lambda \cdot \boldsymbol{R}) \rangle_q$$
$$= -(3P_0/(zR/v)^2)[\cos(zR/v) - \sin(2R/v)/(zR/v)]. \tag{25b}$$

Here, v_p are sound velocities corresponding to the three acoustic branches $p = 1, 2, 3$ of the phonon spectrum; in the last expression, we have set, for the sake of simplicity, $v_{\text{long}} = v_{\text{trans}} = v$; $\langle \ldots \rangle_q$ denotes the average over the directions of the wavevector $\boldsymbol{q}$, V' is the volume of the crystal, T_0 is the temperature characterizing the strength of the spin-lattice coupling, above which the multiphonon processes become important (Pirc *et al* 1966, Dick 1977, Sander and Shore 1971) and $R = |\boldsymbol{R}|$ is the distance between the TLS in the pair.

In order to get the relaxation rates, we calculate

$$C_4(\omega \pm i\eta) = \mp i\pi J_+(\omega) \coth(\omega/2k_B T)$$
$$= \mp(i\omega/2\pi)[P_0 + P_\omega(R)] \coth(\omega/2k_B T) \tag{26}$$

where we have neglected the real part

$$\oint J_+(z)(\omega - z)^{-1} \coth(z/2k_B T) \, dz.$$

We can write the first factor in (21) at $\omega \pm i\eta$ as

$$[\omega - 2J \pm i W_1(\omega)][\omega + 2J \pm i W_1(\omega)]$$

with $W_1(\omega) = (\Delta^2/\pi)[P_0 + P_\omega(R)] \coth(\omega/2k_B T)$. The Green function $G_{22}(\omega)$ has a resonant behaviour around $\omega = \pm 2J$. So we identify the damping constant $w_1 = W_1(\omega = 2J)$ with the inverse relaxation time, thus obtaining

$$W_1 = (2\Delta^2 J/\pi)[P_0 + P_{2J}(R)] \coth(J/k_B T). \tag{27a}$$

In a similar manner, we find, from the second factor in (21), the other relaxation rate

$$W_2 = (2\Delta^4/\pi J^2)[P_0 - P_{2\Delta^2/J}(R)] \coth(\Delta^2/k_B TJ). \tag{27b}$$

The approximations made in arriving at the expressions (27) result in giving the same results as obtained from the golden rule calculation.

5. Conclusions

In the present article, the dynamics of pairs of coupled two-level tunnelling systems has been studied, and longitudinal susceptibility and the relaxation rates for reorientational processes of pairs have been calculated.

In view of the fact that two-level centres have been studied in the present paper, results of our calculation cannot be compared directly, in a quantitative way, with those obtained experimentally by studying more complex multilevel systems. The calculations give, however, better and more complete insight into the rather complicated mechanism of the behaviour of coupled pairs of centres.

The experiments performed by Potter and Anderson (1981) and Moy *et al* (1983) could be explained by the assumption of simultaneous reorientation of coupled pairs of centres. There is, therefore, an intermediate range of concentration of the centres—between the dilute limit where no cooperative features appear, and the higher concentration case where large clusters of interacting tunnelling units are formed to determine the macroscopic properties of the material—where the formation of pairs of interacting centres manifests itself through some observable macroscopic properties. It could be speculated that after pairs, in addition triples, four-member clusters and so forth are formed. As the effects due to pairs go as the square of the concentration, and those due to triples as the third power, etc. it may not be possible, however, to detect the small clusters, with exception of pairs, because it is the very large clusters which begin to govern the behaviour of the system of the centres before the concentration grows sufficiently high for the smaller clusters to be detectable.

It is therefore possible that the dynamics of pairs of coupled centres might have some special importance as the only detectable (or at least the only one detected up to now) intermediate step between the system of isolated centres and the system of interacting centres.

Appendix A

Let us denote

$$\mathcal{G}^i_{KL}(\omega) = \langle\!\langle \hat{A}_i S_K ; S_L \rangle\!\rangle \qquad i = 1, 2. \tag{A.1}$$

The equation of motion for $\mathbf{G}(\omega)$ can then be written

$$\omega \mathbf{G}(\omega) = \mathbf{K} + \mathbf{M}\mathbf{G}(\omega) + 2i\Delta \sum_{i=1}^{2} \mathbf{N}^i \mathcal{G}^i(\omega) \tag{A.2}$$

where $\mathbf{G}$, $\mathcal{G}^i$ and $\mathbf{K}$ are matrices with elements G_{KL}, $\mathcal{G}^i_{KL}$ and $K_{KL} = \langle [S_K, S_L] \rangle$, respectively. The matrix $\mathbf{M}$ may be written as a direct sum

$$\mathbf{M} = \mathbf{M}_1 \oplus \mathbf{M}_1 \oplus \mathbf{M}_2 \oplus \mathbf{M}_3 \oplus \mathbf{0}_2 \tag{A.3}$$

$$\mathbf{M}_1 = \begin{vmatrix} 0 & 2i\Delta & -2iJ & 0 \\ -2i\Delta & 0 & 0 & 0 \\ 2iJ & 0 & 0 & -2i\Delta \\ 0 & 0 & 2i\Delta & 0 \end{vmatrix}$$

$$\mathbf{M}_2 = \begin{vmatrix} 0 & 2iJ \\ -2iJ & 0 \end{vmatrix}$$

$$\mathbf{M}_3 = \begin{vmatrix} 0 & 2\mathrm{i}J & 0 \\ -2\mathrm{i}J & 0 & 4\mathrm{i}\Delta \\ 0 & -4\mathrm{i}\Delta & 0 \end{vmatrix}$$

and $\mathbf{0}_2\ (\mathbf{0}_n)$ is a two- (n-) dimensional null matrix. The matrices $\mathbf{N}^j, j = 1, 2$, are

$$\mathbf{N}^j = \begin{vmatrix} \mathbf{0}_8 & \mathrm{i}\mathcal{N}^j \\ -\mathrm{i}(\mathcal{N}^j)^T & \mathbf{0}_7 \end{vmatrix}$$

where $\mathcal{N}^{1,2}$ are rectangular 8×7 matrices

$$\mathcal{N}^{1,2} = \begin{vmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \pm 1 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & -1 & 2 \\ 0 & \pm 1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & \pm 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mp 1 & \mp 1 & \mp 2 \\ 0 & 1 & 0 & \mp 1 & 0 & 0 & 0 \end{vmatrix}.$$

The matrices $\mathbf{N}^j$ are Hermitian.

In solving equation (A.2), we apply to the higher-order Green functions the Tyablikov decoupling scheme (15). To obtain $\mathcal{G}^j_{KL}$, one needs $\langle\langle a_\lambda S_K ; S_L \rangle\rangle_\omega$ and $\langle\langle a^+_\lambda S_K ; S_L \rangle\rangle_\omega$.

The equation of motion for $\langle\langle a_\lambda S_K ; S_L \rangle\rangle_\omega$, if the decoupling scheme (15) is applied and performed to the second order, is found to be

$$(\omega - \omega_\lambda)\langle\langle a_\lambda S_K ; S_L \rangle\rangle_\omega = \sum_R M_{KR}\langle\langle a_\lambda S_R ; S_L \rangle\rangle_\omega + \mathrm{i}\Delta[\mathcal{M}_\lambda \mathbf{G}(\omega)]_{KL}. \tag{A.4}$$

M_{KL} are elements of the matrix $\mathbf{M}$ given by (A.3), and the Hermitian matrix $\mathcal{M}_\lambda$ is equal to

$$\mathcal{M}_\lambda = \sum_{j=1}^{2} \gamma_{j\lambda}(2\bar{n}_\lambda + 1)\mathbf{N}^j. \tag{A.5}$$

In determining $\mathcal{M}_\lambda$, proper symmetrization had to be performed.

From equation (A.4) and an analogous equation for $\langle\langle a^+_\lambda S_K ; S_L \rangle\rangle_\omega$, one finds the relationship between $\mathcal{G}^j(\omega)$ and $\mathbf{G}(\omega)$

$$\mathcal{G}^j(\omega) = \mathrm{i}\Delta \sum_\lambda [(\omega - \omega_\lambda - \mathbf{M})^{-1}(\gamma^*_{j\lambda}\mathcal{M}_\lambda) - (\omega + \omega_\lambda - \mathbf{M})^{-1}(\gamma_{j\lambda}\mathcal{M}^*_\lambda)]\mathbf{G}(\omega)$$

and finally, from equation (A.2), equation (16) is obtained where

$$\mathbf{B}^j(\omega) = 2\Delta^2 \mathbf{N}^j \sum_\lambda [(\omega - \omega_\lambda - \mathbf{M})^{-1}(\gamma^*_{j\lambda}\mathcal{M}_j) - (\omega + \omega_\lambda - \mathbf{M})^{-1}(\gamma_{j\lambda}\mathcal{M}^*_\lambda)]. \tag{A.6}$$

The matrix $\omega - \mathbf{M} - \Sigma_j \mathbf{B}^j$ may again be written as a direct sum

$$\omega - \mathbf{M} - \sum_{j=1}^{2} \mathbf{B}^j(\omega) = \mathbf{C}^+(\omega) \oplus \mathbf{C}^-(\omega) \oplus \mathbf{C}'(\omega) \tag{A.7}$$

the block form of the matrix (A.7) means that the 'configurational space' of the spin coordinates splits into three direct product subspaces. The first two have dimension

4. As we are primarily interested in $\langle\langle\sigma_k^z; \sigma_l^z\rangle\rangle_\omega$, only $\mathbf{C}^\pm$ need be known. $\mathbf{C}^\pm$ are the following 4×4 matrices:

$$\mathbf{C}^\pm = \begin{vmatrix} \omega & -2\mathrm{i}\Delta & 2\mathrm{i}J & 0 \\ 2\mathrm{i}\Delta & \omega-4\Delta^2 C_1^\pm & -4\Delta^2 C_2^\pm & -4\mathrm{i}\Delta^2 C_3^\pm \\ -2\mathrm{i}J & -4\Delta^2 C_2^\pm & \omega-4\Delta^2 C_4^\pm & 2\mathrm{i}\Delta(1+2\Delta C_5^\pm) \\ 0 & 4\mathrm{i}\Delta^2 C_3^\pm & -2\mathrm{i}\Delta(1+2\Delta C_5^\pm) & \omega-4\Delta^2 C_6^\pm \end{vmatrix} \tag{A.8}$$

$$C_2^\pm = 8\Delta J \sum_\lambda S_{E,\lambda}(\mathcal{H}_\lambda^0 \pm \mathcal{H}_\lambda^1)$$

$$C_3^\pm = 2J \sum_\lambda [(R_{J,\lambda} - R_{E,\lambda})\mathcal{H}_\lambda^0 \mp (R_{J,\lambda} + R_{E,\lambda})K_\lambda^1]$$

$$C_4^\pm = \sum_\lambda \left[(Q_{E,\lambda} - 4J^2 S_{E,\lambda}) + 3\left(\frac{1}{\omega+\omega_\lambda} + \frac{1}{\omega-\omega_\lambda}\right)\right](\mathcal{H}_\lambda^0 \pm \mathcal{H}_\lambda^1)$$

$$C_5^\pm = 4\Delta \sum_\lambda R_{E,\lambda}(\mathcal{H}_\lambda^0 \pm \mathcal{H}_\lambda^1) \tag{A.9}$$

$$C_6^\pm = \sum_\lambda [(Q_{J,\lambda} + Q_{E,\lambda})\mathcal{H}_\lambda^0 \mp (Q_{J,\lambda} - Q_{E,\lambda})\mathcal{H}_\lambda^1]$$

$$C_1^\pm = C_6^\pm - (2\Delta/J)C_2^\pm$$

$$Q_{T,\lambda}(\omega) = (\omega+\omega_\lambda)[(\omega+\omega_\lambda)^2 - 4T^2]^{-1} + (\omega-\omega_\lambda)[(\omega-\omega_\lambda)^2 - 4T^2]^{-1}$$

$$R_{T,\lambda}(\omega) = [(\omega+\omega_\lambda)^2 - 4T^2]^{-1} + [(\omega-\omega_\lambda)^2 - 4T^2]^{-1} \tag{A.10}$$

$$S_{T,\lambda}(\omega) = \{(\omega+\omega_\lambda)[(\omega+\omega_\lambda)^2 - 4T^2]\}^{-1} + \{(\omega-\omega_\lambda)[(\omega-\omega_\lambda)^2 - 4T^2]\}^{-1}$$

$$T = J, E \qquad E = \sqrt{J^2 + 4\Delta^2}$$

$$\mathcal{H}_\lambda^0 = |\gamma_\lambda|^2(2\bar{n}_\lambda + 1)$$

$$\mathcal{H}_\lambda^1 = \tfrac{1}{2}(2\bar{n}_\lambda + 1)(\gamma_{1\lambda}\gamma_{2\lambda}^* + \gamma_{1\lambda}^*\gamma_{2\lambda}) = |\gamma_\lambda|^2(2\bar{n}_\lambda + 1)\cos(\mathbf{q}_\lambda \cdot \mathbf{R})$$

where $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, $\mathbf{R}_1$ and $\mathbf{R}_2$ being positions of the two interacting TLS. For convenience of writing, the argument has been dropped in $C_j^\pm(\omega)$ for $j=1$ to 6, and in $Q_{T,\lambda}(\omega)$, $R_{T,\lambda}(\omega)$ and $S_{T,\lambda}(\omega)$ in (A.9).

References

Anderson P W, Halperin B I and Varma C M 1972 *Phil. Mag.* **25** 1
Bridges F 1975 *Crit. Rev. Solid State Sci.* **5** 1
Dick B G 1977 *Phys. Rev. B* **16** 3359
Hunklinger S and Raychaudhuri A K 1986 *Prog. Low Temp. Phys.* **9** 265
Junker W and Wagner M 1981 *Solid State Commun.* **40** 383
Klein M W 1984 *Phys. Rev. B* **29** 5825
Kranjc T 1990 *Proceedings Phonons 89* ed S Hunklinger, W Ludwig and G Weiss (Singapore: World Scientific) p 591
Moy D, Potter R C and Anderson A C 1983 *J. Low Temp. Phys.* **52** 115
Nakajima S, Toyozawa Y and Abe R 1980 *The Physics of Elementary Excitations (Springer Series in Solid-State Sciences 12)* (Berlin: Springer)
Narayanamurti V and Pohl R O 1970 *Rev. Mod. Phys.* **42** 201
Parry W E and Turner R E 1969 Green functions in statistical mechanics *Many-Body Problems, Progress in Physics* (New York: Benjamin)
Phillips W A 1972 *J. Low Temp. Phys.* **7** 351

—— 1981 *Amorphous Solids* (Berlin: Springer)
Pirc R, Žekš B and Gosar P 1966 *J. Phys. Chem. Solids* **27** 1219
Potter R C and Anderson A C 1981 *Phys. Rev.* B **24** 677
—— 1981 *Phys. Rev.* B **24** 4826
Sander L M and Shore H B 1971 *Phys. Rev.* B **3** 1472
Sethna J P 1981 *Phys. Rev.* B **24** 698
Sethna J P and Chow K S 1985 *Phase Transitions* **5** 317
Zubarev D N 1960 *Usp. Fiz. Nauk* **71** 71 (Engl. Transl. 1960 *Sov. Phys.–Usp.* **3** 320)