(A) DYNAMICS OF A "CENTRAL SPIN"

From now on we will be interested in the general problem of a network of interacting spins, and the interesting quantum magnetic phenomena that can arise therein. We will see that quantum mechanical effects are most obvious when classical effects are suppressed, and that there are 2 ways of doing this. One of these is to "frustrate" the classical ordering, either by using geometrical constraints or by having several magnetic couplings which lead to mutually incompatible classical states (or even better, using both of these!). The other way is to suppress the interaction between the spin system and the "quantum environment" with which it interacts - this environment tends to favor rather strongly classical ordering.

To better understand the latter mechanism we need a much better understanding of the interaction between a spin and its environment, and how the environment affects the spin dynamics. This is the subject of the present section.

A.1. CENTRAL SPIN: EFFECTIVE HAMILTONIAN

Consider a single spin system, which is isolated in a non-magnetic matrix. We will assume that this matrix can be either conducting or insulating, and we will assume that the "central spin" system can either be a single paramagnetic spin system, or some "cluster" or "molecule", ie., a composite spin system. We wish to have a correct description of this system in the form of an effective Hamiltonian, valid for a variety of energy scales.

Note that there is a huge variety of physical systems we could be describing with this kind of model. Some examples are:

- A paramagnetic spin "impurity" in a non-magnetic 3-d matrix, on a 2-d non-magnetic surface or film, or attached to some 1-d non-magnetic chain or "quantum wire". The 3-d and 2-systems would typically be non-magnetic insulators or semiconductors, or metallic systems - but the spins could also be embedded in v. large 3-d or 2-d non-magnetic molecules. As specific examples of some of these, one can consider a TM ion (Fe, Co, Ni, Mn, etc) in some metallic host, described by a Kondo or Anderson Hamiltonian; or a RE impurity like Ho or Tb in a non-magnetic matrix, described by a standard "spin Hamiltonian"; or magnetic TM ions in a large insulating & non-magnetic biomolecule (eg., Fe ions in haemoglobin); or TM ions on a metallic surface, in an STM experiment; or TM spin attached to insulating organic non-magnetic chain molecules (like, eg., TTF-TCNQ chains).

- A large-spin "magnetic molecule" (typically composed of c. 5-100 individual magnetic ions, coupled together by superexchange interactions, and containing in addition a large number of other non-magnetic "ligand" ions, which are often organic groups). This molecule can be embedded in a non-magnetic matrix or on a non-magnetic surface, or else attached to non-magnetic chains. Because the ligands are usually organic, it is usually easiest to embed or attach the molecule to some organic matrix, film, or chain system; but one can imagine connecting to a semiconducting or metallic system. Note that these molecules can assume a bewildering variety of shapes and sizes, with an equally complex assortment of orderings. One has rings, spheres, truncated ladders, onion structures, etc., etc. Well-known examples: Fe-8, Mn-12, V-15, Fe rings.

— A metallic nanomagnetic particle, containing 10-1000 individual TM or RE magnetic ions coupled by FM exchange interactions. Such particles can be embedded in conducting or insulating non-magnetic matrices (eg., Mn or Co particles in Cu) or on metallic or conducting surfaces (eg Co particles on a "magnetic tape", or Er particles on a semiconductor in a semiconducting laser). They can also be attached to or embedded in 1-d conductors in a relatively new field of nanoscience - these conductors include 1-d quantum wires, nanotubes, etc...

We take each of these categories in turn, and discuss what kind of effective Hamiltonian we expect for them. An important note - the kinds of system we can include do not necessarily have to be magnetic. Many small systems have effective Hamiltonians that can be written as though they were quantum spin systems, with a finite-dimensional Hilbert space having a set of discrete levels. Well-known examples include defects in solids (in 3-d, 2-d, or even 1-d systems), and various kinds of non-magnetic impurity. We also describe these systems below.

A.1.1 PARAMAGNETIC SPIN COUPLED TO NON-MAGNETIC SYSTEM

At the microscopic level, the description of a PM impurity coupled to a non-magnetic matrix can be given using standard theory, with effective Hamiltonians which depend on the energy scale of interest. The Hamiltonians that are conventionally used depend typically on whether the system is insulating or conducting. However, the initial stages of forming an effective Hamiltonian do not depend on this

(a) High-Energy Hamiltonian : At high energies, $> 1\,eV$, we start from an Anderson model for the impurity coupled to the surroundings, with Hamiltonian

$$\left.\begin{aligned} \mathcal{H}_{And} = & \sum_{m\sigma} E_m d^{+}_{m\sigma} d_{m\sigma} + \sum_{j\ell\sigma} \epsilon^{0}_{j\ell} c^{+}_{j\ell\sigma} c_{j\ell\sigma} + \sum_{\ell m} \sum_{\sigma} \left[V_{j\ell}(m)\, c^{+}_{j\ell\sigma} d_{m\sigma} + H.c. \right] \\ & + \sum_{\substack{ij \\ \ell\ell'\sigma}} \left[t^{\ell\ell'}_{ij} c^{+}_{i\ell\sigma} c_{j\ell'\sigma} + H.c. \right] + \frac{1}{2} \sum_{j} \sum_{\substack{\ell\ell' \\ \sigma\sigma'}} \left[U^{p}_{j\ell} \delta_{\ell\ell'} \delta_{\sigma,-\sigma'} + U^{p}_{\ell\ell'} \right] n^{\sigma}_{j\ell} n^{\sigma'}_{j\ell'} \\ & + \frac{1}{2} \sum_{\substack{mm' \\ \sigma\sigma'}} \left[U^{d}_{m} \delta_{mm'} \delta_{\sigma,-\sigma'} + U^{d}_{mm'} \right] n^{\sigma}_{0}(m)\, n^{\sigma'}_{0}(m') \\ & + \{ V_{ph} + V_{Hyp} + V_{EM}) \end{aligned}\right\} \quad (1)$$

Here the PM ion is at the origin, and we are interested in the coupling between the quasi-localised d levels (with energies E_m for sub-orbital $|m\rangle$) and their surroundings. The surroundings include (i) a set of more delocalised "sp"-electrons, with atomic energies ϵ^{0}_{ℓ} and hopping amplitudes $t^{\ell\ell'}_{ij}$ between orbitals $|\ell\rangle, |\ell'\rangle$ on separate sites i and j; and (ii) baths of phonons, nuclear spins, and photons whose couplings to the local system we consider below. Note that we could use a similar form to describe RE ions in an insulating matrix, with f-electrons instead of d-electrons. We also incorporate on-site Coulomb interactions in the Hubbard form of U^p and U^d terms for electrons in sp- or d-orbitals. No distinction is made in the sum over sites j between the local site at the origin, and all the other sites. We have dropped the spin-orbit coupling from (1), but it will be included below.

In general the energies ϵ^0_{jl} and the hopping matrix elements $t^{ll'}_{ij}$ will be different depending on whether the site at the origin is involved. This is because the sp-orbitals on the central site will in general be different from those on the sites in the surrounding matrix. In the same way, the on-site repulsions U^p_{jl} and $U^p_j(ll')$ will be different on the local "central spin" site.

A simplified version of (1) is often used.

$$\left.\begin{aligned}\mathcal{H}_{And} = \sum_{m\sigma} E_m d_{m\sigma} + \sum_{kn\sigma} \epsilon_{kn} C^{+}_{kn\sigma} C_{kn\sigma} + \sum_{m}\sum_{kn\sigma} \left[V^{m}_{\underline{k}n} C^{+}_{kn\sigma} d_{m\sigma} + H.c \right] \\ + \frac{1}{2} \sum_{\substack{mm' \\ \sigma\sigma'}} \left[U^d_m \delta_{mm'} \delta_{\sigma,-\sigma'} + U^d_{mm'} \right] n^{\sigma}_{0m} n^{\sigma'}_{0m'} \\ + \left(V_{ph} + V_{Hyp} + V_{EM} \right)\end{aligned}\right\} \quad (2)$$

in which the description of the s-p bands has been simplified considerably - we make the substitution

$$\sum_{jl\sigma} \epsilon^0_{jl} C^{+}_{jl\sigma} C_{jl\sigma} + \sum_{\substack{ij \\ ll'\sigma}} \left[t^{ll'}_{ij} C^{+}_{il\sigma} C_{jl\sigma} + H.c \right] + \frac{1}{2} \sum_{j} \sum_{\substack{ll' \\ \sigma\sigma'}} \left[U^p_{jl} \delta_{ll'} \delta_{\sigma,-\sigma'} + U^p_{ll'} \right] \times n^{\sigma}_{jl} n^{\sigma'}_{jl'}$$

$$\longrightarrow \sum_{kn\sigma} \epsilon_{kn} C^{+}_{kn\sigma} C_{kn\sigma} \quad (3)$$

and modify the hybridisation term $V^m_{jl} \to V^m_{\underline{k}n}$ accordingly. The band energy is then given by assuming $l \equiv n$

$$\left.\begin{aligned}\epsilon_{kn} \sim \epsilon^0_{jn} + \sum_{j \neq i} \left[t^{nn'}_{ij} \delta_{nn'} e^{i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} + H.c \right] \\ + \sum_{n'\sigma'} \left\langle \left(U^p_{jn} \delta_{nn'} \delta_{\sigma,-\sigma'} + U^p_{nn'} \right) n^{\sigma'}_{jn'} \right\rangle\end{aligned}\right\} \quad (4$$

where the average over the local interaction is done using some approximation (the simplest being a HFA; band-structure calculations now use much more sophisticated methods).

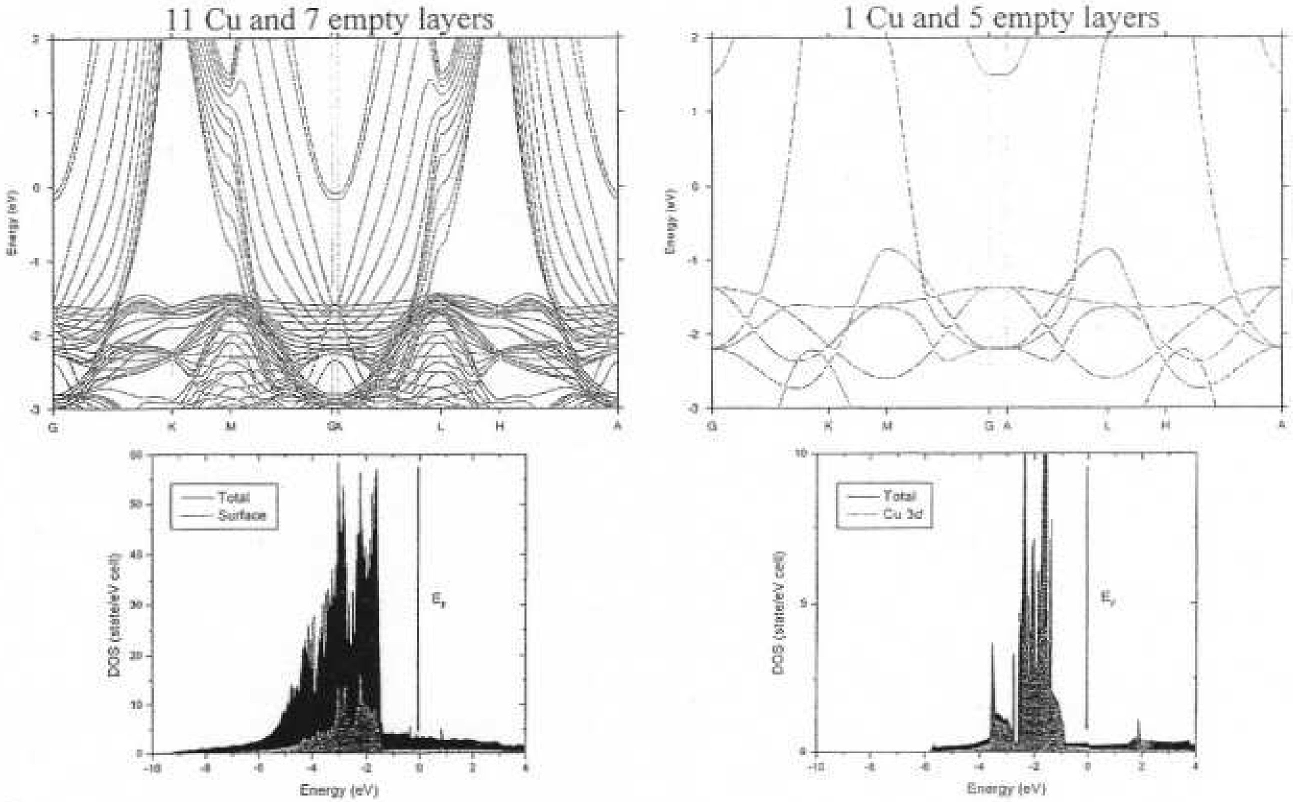
It is possible at this point to also incorporate the spin-orbit coupling, added now at the microscopic level in the form

$$V^{so}_{mm'\sigma} = \frac{-\gamma_c}{2m} \int d^3r\, \psi^{*}_{m\sigma} \frac{\hbar}{2} \sigma \cdot \left[\nabla_r V(\underline{r}) \times i\hbar \nabla_r \right] \psi_{m\sigma}(\underline{r}) \quad (5)$$

to either (1) or (2). This is how it is done in detailed band calculations, or equivalent numerically intensive schemes.

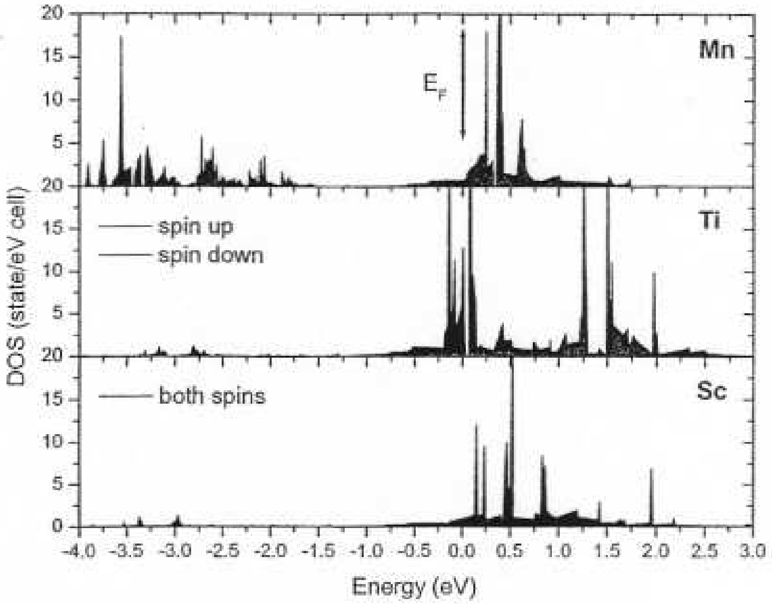
It is actually quite interesting to see what sort of results come out of such numerical calculations. The Figures below show what one gets when computing the level structure for a single TM ion coupled to a 2-d monolayer of Cu. Note first that the band structure for Cu in 2d is rather different from that in 3-d, as we see by comparing the structure shown below with a 3-d band structure.

Cu (111) surface



Sc, Ti and Mn on Cu (111) one monolayer

3d partial density of states (3x3 scell)



Number of d-electrons	Mag. moment (μ_B)
5.37	4.20
2.35	1.79
1.25	0.0

ABOVE: THE BAND STRUCTURE & THE DENSITY OF STATES FOR 2-d Cu FILMS; AN 11-ATOM THICK LAYER IS AT LEFT, AND A SINGLE MONOLAYER AT RIGHT.

BELOW: THE EXTRA DENSITY OF STATES CONTRIBUTION FROM VARIOUS TM IONS ON A Cu MONOLAYER.

(b) Low-Energy Spin Hamiltonian (Insulating Matrix) : Now let us look more closely at the effective spin Hamiltonian we get when we go to lower energies, at the same time assuming our PM spin is coupled to a background insulating "substrate" or matrix.

The net effect of the spin-orbit coupling and crystal fields operating on the central ionic d- or f-orbitals may or may not be simple, depending on where the Fermi energy ends up with respect to these levels. If we assume that ϵ_F is well away from the delocalised sp-bands of the host matrix, and that the PM impurity is not forced into any kind of fluctuating valence state, then we can argue that the PM impurity should be described by a standard anisotropic spin Hamiltonian. In the case of TM ions this will take the form (for a system with inversion symmetry):

$$\left.\begin{aligned} \mathcal{H}_{eff}^{K} = K(\underline{S}) &= k^{(2)}_{\alpha\beta}\, \hat{S}_\alpha \hat{S}_\beta + k^{(4)}_{\alpha\beta\gamma\delta}\, \hat{S}_\alpha \hat{S}_\beta \hat{S}_\gamma \hat{S}_\delta + O(S^6) \\ &\equiv \frac{1}{S} K^{(2)}_{\alpha\beta}\, \hat{S}_\alpha \hat{S}_\beta + \frac{1}{S^3} K^{(4)}_{\alpha\beta\gamma\delta}\, \hat{S}_\alpha \hat{S}_\beta \hat{S}_\gamma \hat{S}_\delta + \cdots \end{aligned}\right\} \quad (6)$$

ie, a polynomial in $\underline{S}$, with powers up to S. The 2nd form in (6) makes each of the coefficients "intensive", ie, independent of S (all other things being equal).

There are other common ways of writing the expansion in (6). One of the more commonly used ones is that used originally by Stevens. Quite generally the form of the terms that are allowed depends on the crystal field symmetry; as we would expect. The lowest quadratic term has the form

$$k^{(2)}_{\alpha\beta} = -\lambda_{so}^2 \sum_\mu \frac{\langle 0|\hat{L}_\alpha|\mu\rangle\langle\mu|\hat{L}_\beta|0\rangle}{E_\mu - E_0} \quad (7)$$

in a system like a TM ion where crystal fields are much larger than the spin-orbit coupling. Here $|\mu\rangle$ are the crystal-field split atomic levels, and λ_{so} is the spin-orbit coupling. The higher powers of S have coefficients which are simply higher-order terms in an expansion of the spin-orbit coupling in the basis of crystal-field levels, so that

$$|k^{(m)}| \sim O\left(\lambda_{so}^m / \Delta_{CF}^{m-1}\right) \quad (8)$$

where Δ_{CF} is the magnitude of the typical crystal field splitting.

In the case of RE ions it is $\underline{J} = \hat{\underline{L}} + \hat{\underline{S}}$ which is the appropriate operator to work with, and we write a similar expansion to (6), in the form

$$\mathcal{H}^{K}_{eff} = K(\underline{J}) = \sum_m k^{(m)}_{\alpha\beta\gamma\ldots}\, \hat{J}_\alpha \hat{J}_\beta \hat{J}_\gamma \cdots \quad (9)$$

The successive terms in this expansion are calculated similarly to those for TM ions, except that we now use the expansion

$$\left.\begin{aligned} \langle J M_J | \mathcal{H}_K^{eff} | J M_J' \rangle = {} & E_J^0\, \delta_{M_J M_J'} + \langle J M_J | \mathcal{H}_{CF} | J M_J' \rangle \\ & + \sum_{J''} \sum_{M_J''} \frac{\langle J M_J | \mathcal{H}_{CF} | J'' M_J'' \rangle \langle J'' M_J'' | \mathcal{H}_{CF} | J' M_J' \rangle}{E_0(J'') - E_0(J)} \\ & + O(\mathcal{H}_{CF}^4) \end{aligned}\right\} \quad (10)$$

where the energies $E_0(J)$, etc., refer to the eigenstates with the spin-orbit coupling included already. The crystal field Hamiltonian can be expanded in spherical harmonics, but provided $\mathcal{H}_{CF}$ does not have appreciable matrix elements between different values of J, we can instead write $\mathcal{H}_{CF}$ purely in terms of operators which are functions of the J-operators; one writes

$$\hat{\mathcal{H}}_{CF} = \sum_{\ell m} B_\ell^m \hat{O}_\ell^m (\underline{J}) \qquad (11)$$

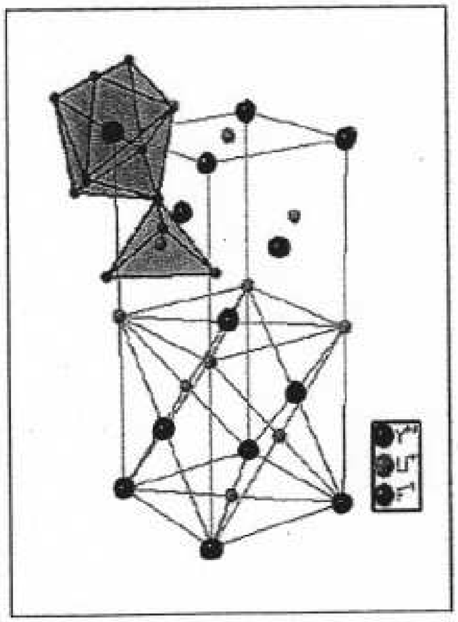
where the "Stevens operators" $\hat{O}_\ell^m(J)$ are proportional to the "tesseral harmonics", and the B_ℓ^m coefficients depend on the form and magnitude of $\mathcal{H}_{CF}$; depending on the symmetry, only some of them will be non-zero. For your interest, the form of the $O_\ell^m(J)$ are listed up to 6-th order in the Table:

RIGHT: FORM OF THE STEVENS OPERATORS UP TO $\sim O(J^6)$ FOR A RE ION.

Stevens operators. $X \equiv J(J+1)$ and $J_\pm \equiv J_x \pm iJ_y$.

$$\begin{aligned}
O_2^2 &= \tfrac{1}{2}(J_+^2 + J_-^2)\\
O_2^1 &= \tfrac{1}{2}(J_zJ_x + J_xJ_z)\\
O_2^0 &= 3J_z^2 - X\\
O_2^{-1} &= \tfrac{1}{2}(J_zJ_y + J_yJ_z)\\
O_2^{-2} &= \tfrac{1}{2i}(J_+^2 - J_-^2)\\
O_4^4 &= \tfrac{1}{2}(J_+^4 + J_-^4)\\
O_4^2 &= \tfrac{1}{4}[(7J_z^2 - X - 5)(J_+^2 + J_-^2) + (J_+^2 + J_-^2)(7J_z^2 - X - 5)]\\
O_4^0 &= 35J_z^4 - (30X - 25)J_z^2 + 3X^2 - 6X\\
O_4^{-2} &= \tfrac{1}{4i}[(7J_z^2 - X - 5)(J_+^2 - J_-^2) + (J_+^2 - J_-^2)(7J_z^2 - X - 5)]\\
O_4^{-4} &= \tfrac{1}{2i}(J_+^4 - J_-^4)\\
O_6^0 &= 231J_z^6 - (315X - 735)J_z^4 + (105X^2 - 525X + 294)J_z^2\\
&\qquad -5X^3 + 40X^2 - 60X\\
O_6^6 &= \tfrac{1}{2}(J_+^6 + J_-^6)
\end{aligned}$$

BELOW: THE STRUCTURE OF THE RE $LiYF_4$ SYSTEM. THE $LiHo_xY_{1-x}F_4$ SYSTEM IS A VERY WELL-KNOWN SPIN GLASS SYSTEM FOR CERTAIN CONCENTRATIONS OF SUBSTITUTED Ho IONS.



Provided the CF terms still conserve J (which they will if $\lambda_{so} \gg \Delta_{CF}$), then all processes caused by $\mathcal{H}_{CF}$ can be described in terms of these operators.

Thus we can also write the Hamiltonian for the RE ion in the non-magnetic matrix as

$$\left.\begin{aligned}\mathcal{H}_{eff} = \sum_{m=0}^{\ell} B_\ell^m \hat{O}_\ell^m(\underline{J}) &- \mu_B J_\alpha g_{\alpha\beta}^J H_0^\beta\\ &+ O(H_0^2)\end{aligned}\right\} \qquad (12)$$

An interesting example to which we shall return is the $LiHo_xY_{1-x}F_4$ system, in which the RE Ho^{3+} ion, with $J = 8$, is surrounded by a "cage" of Li and F⁻ ions. The Ho ion is not only isoelectronic to the Y^{3+} ion, but their atomic volumes are very similar. This means that one can substitute Ho in place of Y without changing the structure.

have an arbitrary concentration x of Ho ions in a $LiYF_4$ matrix without unduly distorting the lattice. We shall return to this system when discussing spin glasses & also magnetic qubits.

As noted above, one also has a coupling between the single magnetic ion and several surrounding "thermal baths", or environments, which themselves are quantum-mechanical. The general form of the hyperfine term is

$$\hat{V}_{Hyp} = \hat{V}^{int}_{Hyp} + V_{NN} \tag{13}$$

$$\left.\begin{aligned} \hat{V}^{int}_{Hyp} &= \tfrac{1}{2}\sum_k A_k^{\alpha\beta} S_\alpha I_k^\beta \\ V_{NN} &= \sum_k Q_k^{\alpha\beta} I_k^\alpha I_k^\beta - g_N^k \mu_N \underline{I}_k \cdot \underline{H}_0 + \tfrac{1}{2}\sum_{kk'} V_{kk'}^{\alpha\beta} I_k^\alpha I_{k'}^\beta \end{aligned}\right\} \tag{14}$$

or the equivalent in terms of J for a RE ion. The nuclear spins $\{\underline{I}_k\}$ both the local magnetic nucleus, and the nuclear spins on sites in the host matrix.

The general form of the spin-phonon term is

$$\left.\begin{aligned} \hat{V}_{ph} = \hbar \sum_{q\lambda} \hbar\omega_q^\lambda \left(a^+_{q\lambda} a_{q\lambda} + \tfrac{1}{2}\right) &+ i \sum_{q\lambda} \underline{q} \cdot \left[g(\underline{S})\, a^+_{q\lambda} - g^+(S)\, a_{q\lambda}\right] \\ &+ O(S^2, a^2). \end{aligned}\right\} \tag{15}$$

with higher-order non-linear phonon terms. Finally, we have coupling to photons. This comes from the basic coupling

$$\mathcal{H}_{EM} = \mu_B(\underline{L} + 2\underline{S}) \cdot \underline{B}(\underline{r},t) + \tfrac{1}{2}\int d^3r \left[\varepsilon_0 |\underline{E}(\underline{r},t)|^2 + \tfrac{1}{\mu_0}|B(\underline{r},t)|^2\right] \tag{16}$$

between the EM field and a spin - we ignore here the electric dipole coupling or higher multipole magnetic couplings. We can quantise the EM field to write this coupling in terms of photon operators - we have

$$\underline{\hat{A}}(\underline{r},t) = \frac{1}{\sqrt{V}} \sum_{qs} \left(\frac{\hbar}{2\omega_q \epsilon_0}\right)^{1/2} \left[a_{qs}\, \underline{\varepsilon}_{qs} + a^+_{qs}\, \underline{\varepsilon}^*_{qs}\right] \tag{17}$$

where we also write photon operators as $\hat{a}_{qs}(\underline{r},t) = \hat{a}_{qs} e^{i(q\cdot r - \omega t)}$, and the polarisation ε_{qs}. Thus we have

$$\left.\begin{aligned} \underline{\hat{E}}(\underline{r},t) &= \frac{i}{\sqrt{V}} \sum_{qs} \left(\frac{\hbar\omega_q}{2\varepsilon_0}\right)^{1/2} \left[a_{qs}\, \underline{\varepsilon}_{qs} - a^+_{qs}\, \underline{\varepsilon}^*_{qs}\right] \\ \underline{\hat{B}}(\underline{r},t) &= \frac{i}{\sqrt{V}} \sum_{qs} \left(\frac{\hbar}{2\varepsilon_0 \omega_q}\right)^{1/2} \left[a_{qs}(\underline{q} \times \varepsilon_{qs}) - a^+_{qs}(\underline{q} \times \varepsilon^*_{qs})\right] \end{aligned}\right\} \tag{18}$$

and we can substitute into (16). We also, using $1/\mu_0\varepsilon_0 = c_0^2$ and $\omega_q = c_0 q$, that the free EM field is just

$$\mathcal{H}^0_{EM} = \tfrac{1}{2} \sum_{qs} \hbar\omega_q \left(a^+_{qs} a_{qs} + a_{qs} a^+_{qs}\right) \tag{19}$$

(c) Low-Energy Spin Hamiltonian (Conducting Matrix): To model a PM spin coupled to a conducting matrix one again starts from the Anderson impurity model in (2). We will discuss (a) under what circumstances this Hamiltonian can be reduced to a Kondo Hamiltonian; and (b) how this can then be transformed to a "spin-boson" model. To give you a feeling for how this would apply to non-trivial real system, the model is then discussed for the real case of a magnetic ion on a 2-d conductor, coupled to an STM tip.

(1) Reduction to Kondo Model. To simplify our discussion we first discuss the single-band, single-orbital Anderson model, i.e., the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + V$, where

$$\left.\begin{aligned} \hat{\mathcal{H}}_0 &= \sum_{k\sigma} \epsilon_k c^+_{k\sigma} c_{k\sigma} + E_d \sum_\sigma d^+_\sigma d_\sigma + \tfrac{1}{2} U \sum_\sigma n^d_\sigma n^d_{-\sigma} \\ &\equiv \sum_{k\sigma} \epsilon_k c^+_{k\sigma} c_{k\sigma} + E_d \sum_\sigma X_0^{\sigma\sigma} + (2E_d + U) X_0^{dd} \end{aligned}\right\} \quad (20)$$

$$\left.\begin{aligned} \hat{V} &= \sum_{k\sigma} \left(V_k c^+_{k\sigma} d_\sigma + H.c \right) \\ &\equiv \sum_{k\sigma} \left[V_k c^+_{k\sigma} \left(X_0^{0\sigma} + \sigma X_0^{-\sigma,d} \right) + H.c. \right] \end{aligned}\right\} \quad (21)$$

where we write the Hamiltonian in terms of Hubbard operators as well. Now we can, in studying the low-energy physics, apply the same canonical transformation techniques to this problem as we did in studying the Hubbard model. We want to find a transformation

$$\hat{\mathcal{H}} \rightarrow \hat{\mathcal{H}}_{eff} = e^{iS} \hat{\mathcal{H}} e^{-iS} \quad (22)$$

in which we have

$$\left.\begin{aligned} &\hat{V} + [i\hat{S}, \hat{\mathcal{H}}_0] = 0 \\ \text{so that} \quad &\mathcal{H}_{eff} = \mathcal{H}_0 + \frac{i}{2}[S, V] \end{aligned}\right\} \quad (23)$$

The way to do this was found by Schrieffer & Wolff in 1966. It is fairly straightforward to implement. We make the ansatz

$$\left.\begin{aligned} \hat{S} &= -i \sum_{k\sigma} \left[V_k \left(\frac{1 - n^d_{-\sigma}}{\epsilon_k - E_d} + \frac{n^d_{-\sigma}}{\epsilon_k - E_d - U} \right) c_{k\sigma} - H.c \right] \\ &\equiv -i \sum_{k\sigma} \left[V_k \left(\frac{X_0^{\sigma 0}}{\epsilon_k - E_d} + \sigma \frac{X^{d,-\sigma}}{\epsilon_k - E_d + U} \right) c_{k\sigma} - H.c. \right] \end{aligned}\right\} (24)$$

(cf the similar transformation for the Hubbard model), to get a whole set of terms. Now in most cases we are interested in, the hybridisation energy scale is much smaller than U, and then we have

$$\mathcal{H}_{eff} = \tilde{\mathcal{H}}_0 + (\mathcal{H}_K + V^{imp}_{sd}) + \text{etc.} \quad (25)$$

where:

$$\tilde{\mathcal{H}}_0 = \mathcal{H}_0 - \sum_{k\sigma} \left(W_{kk} - \tfrac{1}{2} J_{kk} n^d_{-\sigma} \right) n_{d\sigma} \qquad (26)$$

with

$$\left. \begin{aligned} J_{kk'} &= -V_k V_{k'} \left[\frac{1}{\epsilon_k - E_d - U} + \frac{1}{\epsilon_{k'} - E_d - U} - \frac{1}{\epsilon_k - E_d} - \frac{1}{\epsilon_{k'} - E_d} \right] \\ W_{kk'} &= \tfrac{1}{2} V_k V_{k'} \left[\frac{1}{\epsilon_k - E_d} + \frac{1}{\epsilon_{k'} - E_d} \right] \end{aligned} \right\} \qquad (27)$$

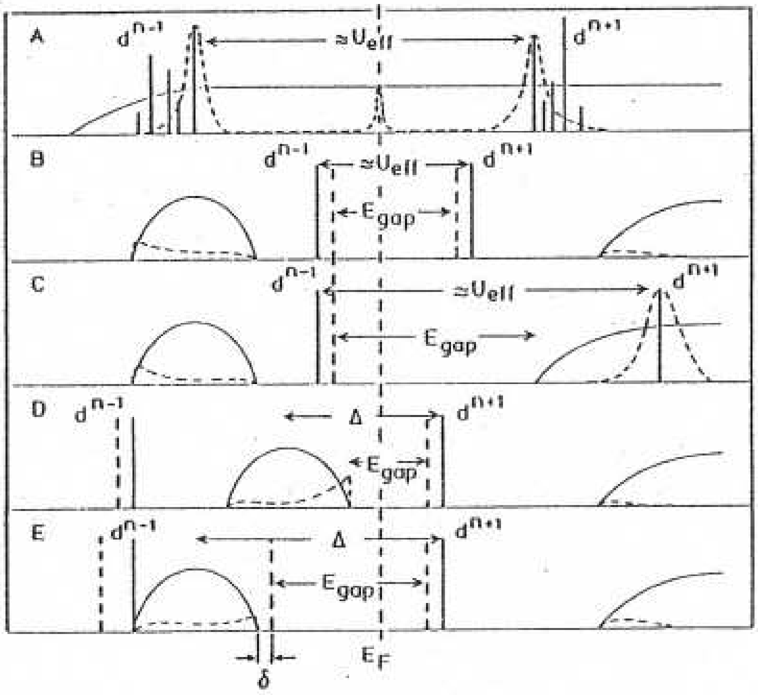
and with the extra terms

$$\mathcal{H}_K = \frac{1}{4} \sum_{kk'} \sum_{\alpha\beta} J_{kk'} \left(c^+_{k\mu} \underline{\sigma}^{\mu\nu} c_{k'\nu} \right) \cdot \left(d^+_\alpha \hat{\underline{\tau}}^{\alpha\beta} d_\beta \right) \qquad (28)$$

$$V^{imp}_{sd} = \sum_{\substack{kk' \\ \sigma\sigma'}} \left[W_{kk'} + \tfrac{1}{4} J_{kk'} d^+_\sigma d_\sigma c^+_{k\sigma'} c_{k\sigma'} \right] \qquad (29)$$

The term $\tilde{\mathcal{H}}_0$ is simply a renormalized version of $\mathcal{H}_0$, with shifts in the energies of the local levels. However the other 2 terms are more interesting. The KONDO term in (28) is an exchange scattering of form $J\underline{S}\cdot\underline{s}$ between the local spin and the conduction electron spins; and the "impurity term" in (29) causes elastic scattering of the conduction electrons off the d-site. There are other terms as well, of lesser importance.

It is very important to understand that this reduction to the Kondo problem is an approximation, and that it is only meaningful in certain cases. Good examples of cases where it is valid are when we have ions like Mn, Co, or Ni, in either 3-d metals like Cu or Au, or on 2-d metallic surfaces of such metals. At left one sees a few of the different possibilities that can arise if we start with the real Anderson model, in eqtn (1). The situation shown in (A) of the figure corresponds to the Kondo model. All of the other correspond to other possibilities.



<u>ABOVE</u>: SPECTRA WHICH RESULT FROM ADDING A SINGLE TM ION TO A BACKGROUND MATRIX. IN (A) WE SEE THE FORMATION OF A KONDO RESONANCE WHEN THE IMPURITY d-ELECTRONS OVERLAP A BROAD CONDUCTION BAND. OTHER SITUATIONS ARISE FOR DIFFERENT VALUES OF U AND OF THE CHARGE TRANSFER Δ.

(ii) The Kondo model & the Spin-Boson model: There is a very simple but rather important model Hamiltonian which is widely used model in physics, which is called the "spin-boson" model. It has the following Hamiltonian, in its most simple form:

$$\mathcal{H}_{SB} = (\Delta \hat{\tau}_x + \epsilon \hat{\tau}_z) + \frac{1}{2}\sum_q \left(\frac{\hat{p}_q^2}{m_q} + m_q \omega_q^2 \hat{x}_q^2 \right) + \sum_q C_q^z \hat{x}_q \hat{\tau}_z \tag{30}$$

In this Hamiltonian, the $\{\hat{p}_q, \hat{x}_q\}$ are canonical coordinates of a set of oscillators, coupled to a 2-level system, or "qubit", which itself has longitudinal & transverse fields acting on it. The qubit also couples to the oscillators via a set of diagonal couplings C_q^z. This is not the most general spin-boson model – one can also have non-diagonal coupling, and a field along the y-axis, giving a term $\epsilon' \hat{\tau}_y$.

It is intuitively obvious that it ought to be possible to map the Kondo problem onto a spin-boson model; ie to have the mapping

$$\mathcal{H}_S = \sum_{k\sigma} \epsilon_k c_{k\sigma}^+ c_{k\sigma} + \mathcal{H}_K \longrightarrow \mathcal{H}_{SB} \tag{31}$$

with the bosons representing electron-hole pairs in the conduction electron bath, and the qubit representing the local Kondo spin. In fact the mapping can be accomplished simply provided we make the following simplification to the Kondo model. First, we assume that the Kondo interaction term can be written as:

$$\mathcal{H}_K \to \frac{1}{4} J_z \hat{\tau}_z \sum_\sigma \sigma c_{0\sigma}^+ c_{0\sigma} + \frac{1}{2} J_\perp (\hat{\tau}_+ c_{0\downarrow}^+ c_{0\uparrow} + \hat{\tau}_- c_{0\uparrow}^+ c_{0\downarrow}) \tag{32}$$

where we write
$$c_{0\sigma} = \frac{1}{\sqrt{V}} \sum_k c_{k\sigma} \tag{33}$$

ie, $c_{0\sigma}^+$ creates an electron of spin σ at the origin. Second, we linearize the electronic spectrum near the Fermi energy:

$$\epsilon_k \to \epsilon_F + \hbar v_F (|k| - k_F) \equiv \epsilon_F + \underline{p}_F \cdot (\underline{k} - \underline{k}_F) \tag{34}$$

The first assumption assumes short-ranged s-wave scattering off the impurity, and the 2nd is a natural consequence of our restriction to low energy scales $\ll \epsilon_F$. One then finds that the mapping (31) is accomplished by identifying (we put $\epsilon = 0$ here).

$$\left.\begin{aligned} \Delta/\Omega_0 &= J_\perp / 4\pi a_0 \Omega_0 \equiv g_\perp \\ \alpha &= (1 - N(0) J_z)^2 \equiv (1 - g_z)^2 \end{aligned}\right\} \tag{35}$$

where we have defined several dimensionless couplings and also a UV cut-off energy Ω_0. The dimensionless Kondo couplings

$$\left.\begin{aligned} g_z &= N(0) J_z \\ g_\perp &= N(0) J_\perp \end{aligned}\right\} \sim 0.1 \tag{36}$$

and the dimensionless spin-boson coupling is defined by looking at the "Caldeira-

Leggett spectral function[*] $J(\omega)$, defined by

$$J(\omega) = \frac{\pi}{2} \sum_q \frac{|C_q^z|^2}{m_q \omega_q} \delta(\omega - \omega_q) \qquad (37)$$

$$\longrightarrow \eta\omega\, \theta(\Omega_0 - \hbar\omega) \qquad \text{("Ohmic" bath)} \qquad (38)$$

and we then define α in terms of the "friction coefficient" η:

$$\alpha = \frac{2\pi h}{a_0^2}\eta \qquad (39)$$

The UV cut-off is assumed much larger than Δ. If we make the assumption $\Omega_0^{-1} = N(0)$ the formulae simplify further. We can easily add back the term $\epsilon\tau_z$; it corresponds in the Kondo problem to an applied magnetic field. Note that $a_0 = \hbar v_F / \Omega_0$.

I only briefly sketch the derivation of these results, since it is a little lengthy. One simple way to do it is to bosonize the fermionic operators – this can be done in a straightforward way because the assumption of s-wave scattering makes the problem a 1-dimensional one. The dimension in question is simply the distance away from the impurity. One then defines boson operators

$$a_q = \left(\frac{\pi}{qL}\right)^{1/2} \rho_{-q} \qquad\qquad b_q = \left(\frac{\pi}{qL}\right)^{1/2} s_{-q} \qquad (40)$$

where

$$\left.\begin{aligned} \rho_q &= \sum_{k\sigma} c^+_{k+q,\sigma} c_{k\sigma} \\ s_q &= \sum_{k\sigma} \sigma\, c^+_{k+q\sigma} c_{k\sigma} \end{aligned}\right\} \qquad (41)$$

where L is the linear size of the system (i.e., $L^3 = V$); note that $\rho_{-q} = \rho_q^+$ and $s_{-q} = s_q^+$, and that $[a_q, a_{q'}^+] = [b_q, b_{q'}^+] = \delta_{qq'}$. The electron gas is then just a set of oscillators:

$$\left.\begin{aligned} \mathcal{H}_{el}^0 &= \hbar v_F \sum_{q>0} \omega_q \left(a_q^+ a_q + b_q^+ b_q\right) \\ \omega_q &= q v_F \end{aligned}\right\} \qquad (42)$$

and using standard bosonization techniques one can show that $\mathcal{H}_K$ in (32) transforms to

$$\left.\begin{aligned} \mathcal{H}_K = {} & \frac{1}{4} J_z \hat{\tau}_z \sum_q \left(\frac{q}{\pi L}\right)^{1/2} \theta(\Omega_0 - \hbar\omega_q)\left(b_q + b_q^+\right) \\ & + \frac{J_\perp}{4\pi a_0}\left[\hat{\tau}_+ e^{\sum_q \left(\frac{4\pi}{qL}\right)^{1/2} \theta(\Omega_0 - \hbar\omega_q)[b_q - b_q^+]} + \text{H.c.}\right] \end{aligned}\right\} \qquad (43)$$

If we then make the canonical transformation $\mathcal{H}_K \to \breve{\mathcal{H}}_K$, with

$$\breve{\mathcal{H}}_K = e^{iS} \mathcal{H}_K e^{-iS}; \qquad S = i\hat{\tau}_z \sum_q \left(\frac{\pi}{qL}\right)^{1/2} \theta(\Omega_0 - \hbar\omega_k)\left[b_q - b_q^+\right] \qquad (44)$$

then we find that

$$\tilde{\mathcal{H}}_K = \Delta\hat{\tau}_x + \hbar\sum_q \omega_q b_q^{+} b_q + \sum_q c_q x_q \hat{\tau}_z \tag{45}$$

provided we assume that

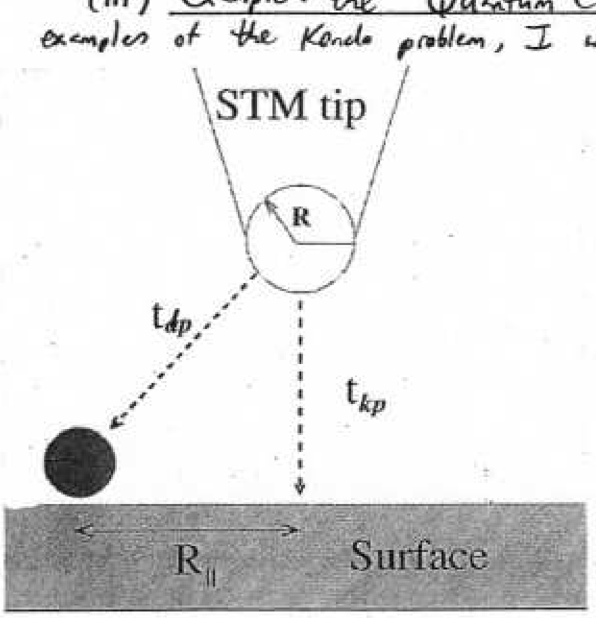
$$\frac{|c_q|^2}{m_q} = \alpha \frac{4}{a_0^2}\left(\frac{2\pi\hbar v_F}{L}\right)\omega_q^2 \;\theta(\Omega_0 - \hbar\omega_q) \tag{46}$$

and make the simple identification

$$x_q = a_0\left(\frac{1}{2\pi\hbar m_q \omega_q}\right)^{1/2}\left[b_q + b_q^{+}\right] \tag{47}$$

Eqtn (45) is nothing but the simple spin-boson model again, in a mixed representation.

(iii) Example: the "Quantum Corral": Rather than pick one of the well-known examples of the Kondo problem, I will pick a more novel 2-d example. Consider the geometry shown at left, in which a particle or atom (which we will assume here to be magnetic) lies on a metallic substrate, and the tip of an STM is brought up close to it. We assume the STM is also metallic, and the gap between STM and the surface is evacuated.



GEOMETRY of the STM EXPT.

The way an STM works is very simple - under an applied voltage between STM tip and surface, electrons tunnel across the gap. The tunneling amplitude is of order

$$t_{kp} \sim t_0 \exp\left[-\frac{2m}{\hbar} W^{1/2} z\right] \tag{48}$$

where t_0 is an "attempt frequency" ($t_0 \sim \epsilon_F$) and W is the work function, ie., W is the difference in energy between a vacuum electron and an electron at the Fermi energy (the metallic analogue of the electron affinity). We see that t_{kp} falls off very rapidly with z, the distance between the tip & surface, since typically $W > 2$ eV.

We can easily write down an effective Hamiltonian for this system in the case where the tunneling electrons must pass through the magnetic ion as well as directly to the surface. We have then

$$\mathcal{H} = \mathcal{H}_{Tip} + \mathcal{H}_S^d + V_{Tip}^S + V_{Tip}^d \tag{49}$$

where the terms are as follows:

The STM tip:

$$\mathcal{H}_{Tip} = \sum_{p\in Tip}\sum_{\sigma} \epsilon_p A_{p\sigma}^{+} A_{p\sigma} \tag{50}$$

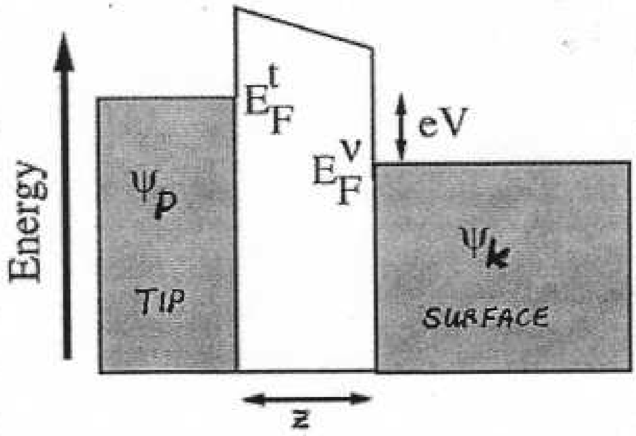
The metal surface + ion:

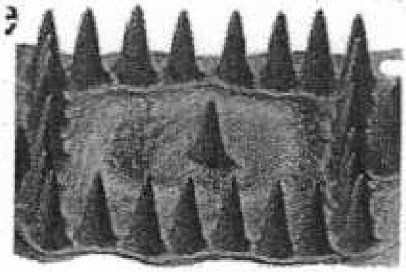
$$\left.\begin{aligned}\mathcal{H}_S^d = {} & \sum_{k\sigma}\epsilon_k c_{k\sigma}^{+} c_{k\sigma} + \sum_m E_m d_{m\sigma}^{+} d_{m\sigma} \\ & + \sum_{km}\left[V_k^m d_{m\sigma}^{+} c_{k\sigma} e^{i\underline{k}\cdot\underline{R}} + H.c.\right] \\ & + \frac{1}{2}\sum_{mm'}\sum_{\sigma\sigma'} U_{mm'}^{\sigma\sigma'} n_{m\sigma} n_{m'\sigma'}\end{aligned}\right\} \tag{51}$$

The surface-tip interaction : $$V^{S}_{Tip} = \sum_{p}\sum_{k\sigma}\left[t_{pk} A^{+}_{p\sigma} c_{k\sigma} e^{ik.r} + H.c \right] \quad (52)$$

The impurity-tip interaction : $$V^{d}_{Tip} = \sum_{p}\sum_{m\sigma}\left[T_{pm}(z,R) A^{+}_{p\sigma} d_{m\sigma} + H.c. \right] \quad (53)$$

In these equations the tip electrons are in rather confined states $|p\sigma\rangle$ where p takes discrete values, with energy ε_p. These can tunnel directly between tip and surface, with amplitude $t_{pk}(z)$, or they can tunnel via the states $|m\sigma\rangle$ on the impurity. The amplitude for this to happen depends very strongly on where the tip is relative to the ion. In an experiment one moves the tip horizontally, and the current rises dramatically as the tip approaches the impurity - it is a very strong function of the horizontal displacement R. Actually one can get a great deal of information from the tunneling current. In a simple 2nd-order

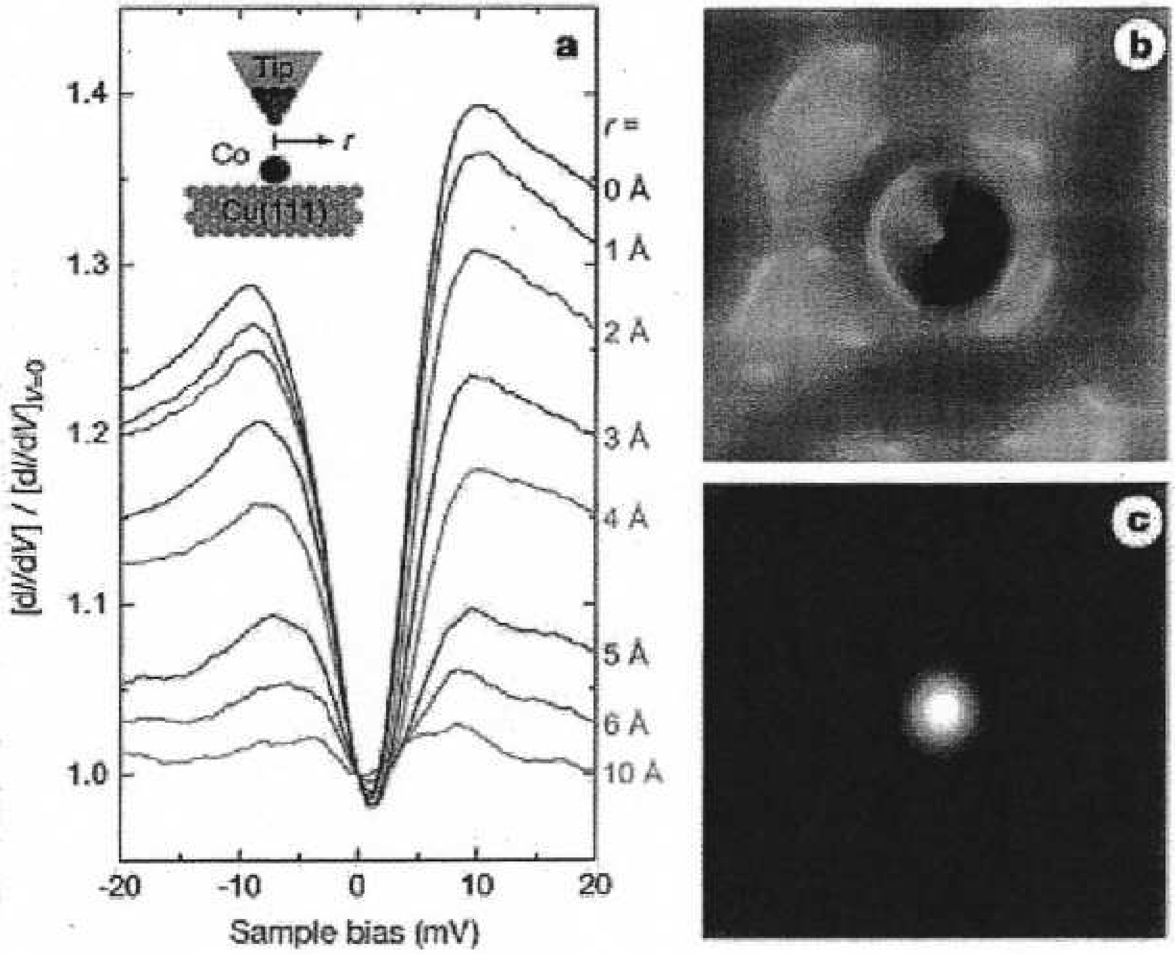




TOP: ENERGETICS INVOLVED IN AN STM EXPT.

LEFT: IMAGE OF A SQUARE "CORRAL" OF Co ATOMS ON A Cu SURFACE, WITH A SINGLE Co ATOM IN THE MIDDLE.

BELOW: MMTS OF dI/dV FOR THE SAME SYSTEM, ALONG WITH IMAGING OF $V(R)$ AND $\delta(dI/dV)(R)$.



perturbation theory treatment of the tunneling current, one expects to find a current

$$I(z,R) = \frac{2\pi e}{\hbar} \sum_{f,i} |M_{fi}|^2 f(\epsilon_i)(1-f(\epsilon_f))\,\delta(\epsilon_i + eV - \epsilon_f) \qquad (54)$$

provided one ignores any interference between different paths (eg., between paths going directly to the surface from the tip, and those going via the ion). It is assumed then that all the $\underline{R}$ dependence is in the matrix element $M_{fi}(z,\underline{R})$, which describes tunneling along the most direct vertical path between tip and what is below it.

$$M_{fi}(z,\underline{R}) \sim \left\{ \begin{array}{ll} \sum_{pk} \psi_{\underline{k}}^*(\underline{R})\, t_{\underline{k}p}\, \Psi_p(\underline{R}) & |\underline{R}| > r_0 \\ \sum_{pd} \phi_d^*(\underline{R})\, T_{dp}\, \Psi_p(\underline{R}) & |R| < r_0 \end{array} \right\} \qquad (55)$$

where $t_{kp}(z)$ and $T_{dp}(z)$ have exponential dependences on z (cf. eqtn (48)), and the wave-function $\Psi_p(\underline{R})$, etc, are given by

$$\left. \begin{array}{llll} \Psi_p(\underline{R}) & = & \langle \underline{R} | \Psi_p \rangle & \text{tip wave-fn.} \\ \phi_d(R) & = & \langle \underline{R} | d \rangle & \text{impurity wave-fn.} \\ \psi_{\underline{k}}(\underline{R}) & = & \langle \underline{R} | \underline{k} \rangle & \text{surface wave-fn.} \end{array} \right\} \qquad (56)$$

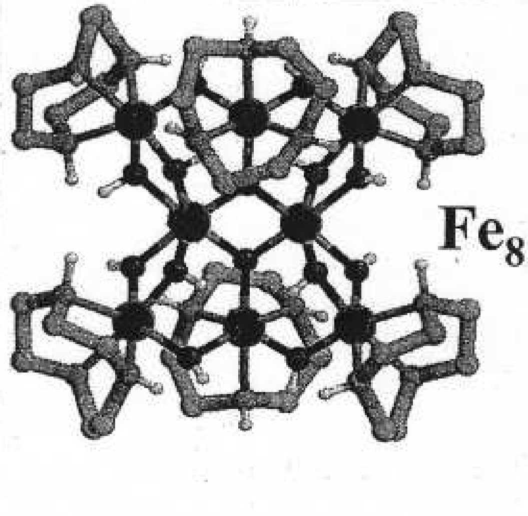
Clearly a more refined theory takes account of the finite "width" of the tube of allowed paths out of the tip, and of interference between those paths going through the ion, & those going directly to the surface.

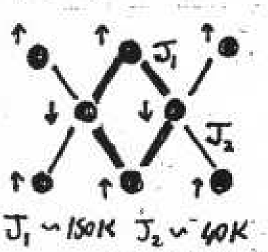
A.1.2. MAGNETIC MOLECULE COUPLED TO NON-MAGNETIC SYSTEM:

The study of molecules containing magnetic ions is a large branch of science, which spans both organometallic and inorganic molecular chemistry. It is now becoming increasingly important in physics, in many different areas - these include strongly-correlated nanoscopic systems, and the study of nanoscopic tunneling phenomena. There are also many current ideas concerning their potential as spin qubits.

To get an idea of what we are talking about, let us look briefly at a few examples: in all cases these molecules are chosen to be insulating.

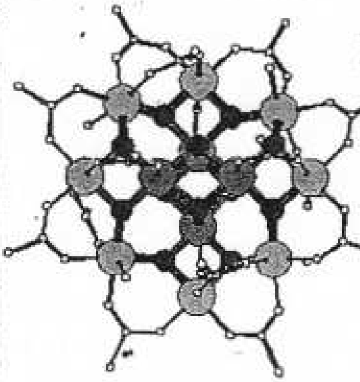
The first example, at left, is the "Fe-8" molecule. It is composed of eight Fe ions, each in a spin-5/2 state, in the simplest model of the system. These are coupled by a variety of AFM superexchange couplings. How these couplings work is shown schematically in the inset at left. One can think of Fe-8 as a "truncated spin ladder", in which a kind of geometrical frustration forces the



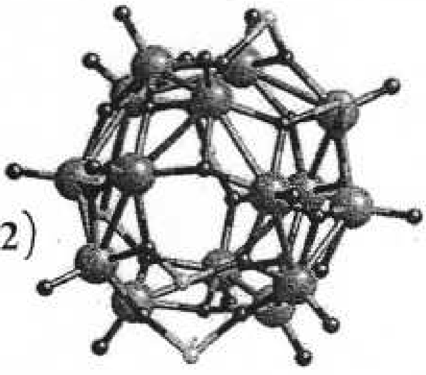


$J_1 \sim 150K$ $J_2 \sim 60K$
DOMINANT COUPLINGS
IN Fe-8 MOLECULE

system into a final $S = 10$ state. In fact Fe-8 is only one of a very large number of what are usually called "SMMs" (Single Molecule Magnets). An selection of some of the genuinely nanoscale (~ 1 nm) is shown below:



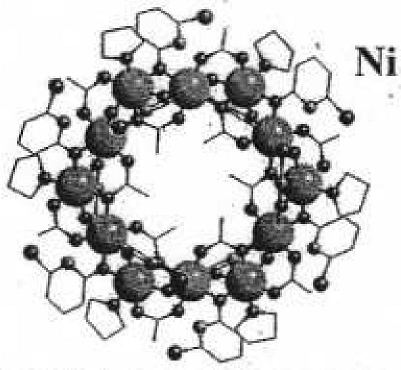
Mn_{12} ($S = 10$)



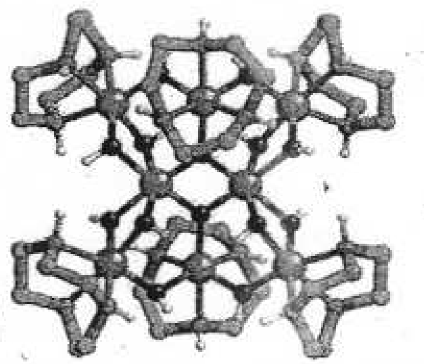
V_{15} ($S = 1/2$)

Single-molecule magnets (SMM)

Giant spins



Ni_{12} ($S = 12$)



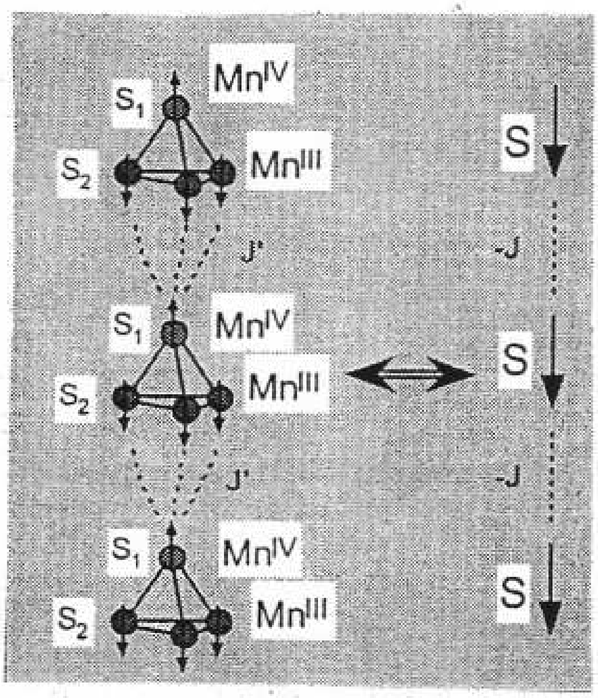
Fe_8 ($S = 10$)

There are roughly 5000 SMM's currently being studied: this is a huge field of chemistry. The "medium-small" size ones shown show some of the variety that exists at this scale:

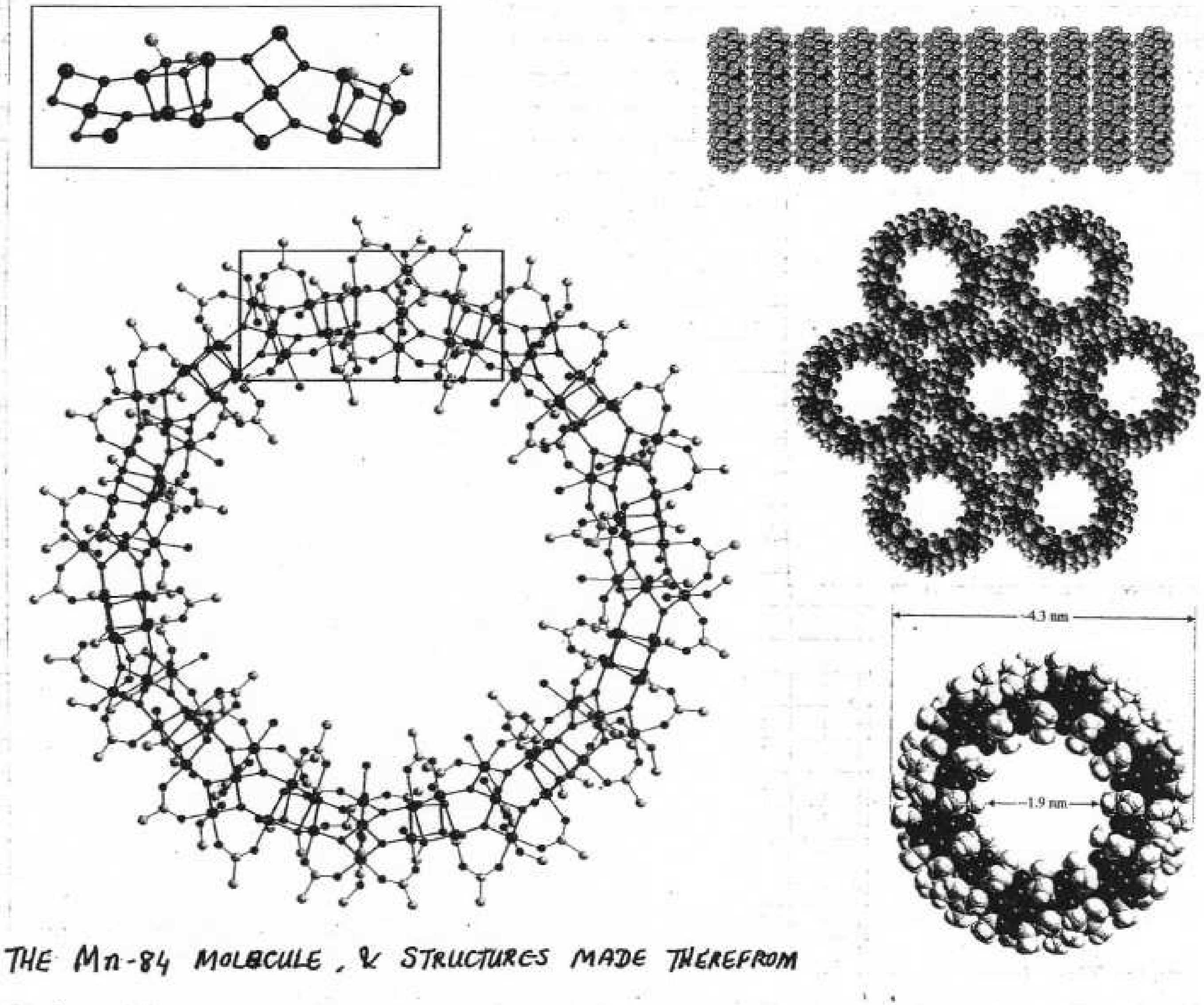
- The Mn-12 molecule has an inner core of 4 spin-$3/2$ Mn^{4+} ions, with a surrounding shell of 8 spin-2 Mn^{3+} ions. The inner core spins are oriented oppositely to the surrounding shell, and so we get a total spin of 10. It is interesting to see how this happens - we discuss this below. The 12 Mn ions are surrounded by organic ligands, as shown.
- The V-15 molecule is made from 15 spin-$1/2$ V ions, organized in 2 hexagons with a triangle in between. The net result, discussed in more detail below, is a system of 3 spin-$1/2$ systems interacting via rather weak (~ 0.5 K) superexchange interactions - a perfect triangle.
- The Ni-12 system is made from 12 Ni spin-1 ions, coupled like all of these systems by superexchange interactions of AFM sign. Long chains of spin-1 Ni ions constitute one of the classic examples of Haldane gap chains. These small rings are nano-examples of these, with no ends and periodic boundary conditions.

One can also have much larger ring systems - the "Mn-84" system is shown on the next page - and it is easy to make superstructures of these (some the architectures that have been made are quite fantastic). One can also make rather smaller basic units, as we see in the case of the Mn_4 molecules seen here at right. An interesting and important thing about these Mn_4 molecules, which have spin-9/2 and the structure shown, is that they can have their interactions and structure organised so that they form chains in which "exchange dimers" form as shown. To do this one needs to remove much of the outer ligand sheath that is formed around many of these molecules, which otherwise make the exchange interactions negligible.

These are real advantages to having the outer ligand shell. It stabilizes the the inner spin structure, and protects it from the outside. One can imagine forming many different structures from these sub-units, whilst maintaining the integrity of the spin structure. Thus one can form chains, 2-d structures or networks on surfaces, or 3-d networks. The ligand shell then allows remarkable nano-engineering possibilities.



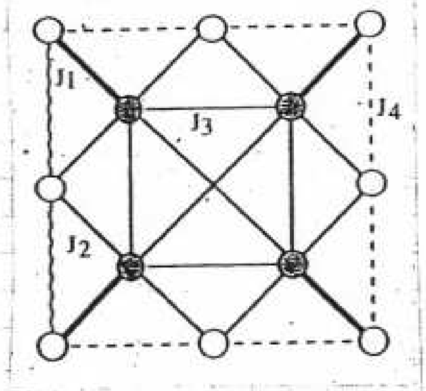
CHAIN STRUCTURE of Mn_4 MOLECULES

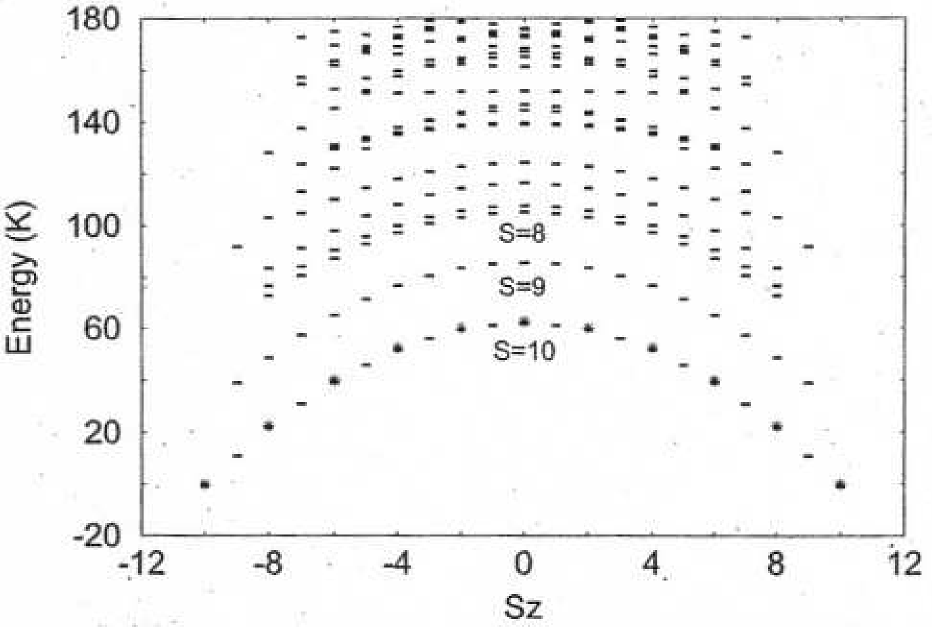


THE Mn-84 MOLECULE, & STRUCTURES MADE THEREFROM

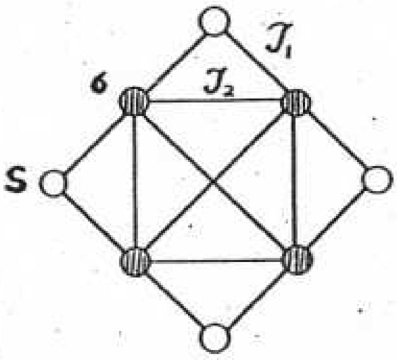
Clearly the actual spin structure of one of these molecules will be very complex. As an example, we consider the Mn-12 molecule shown on page 15. The structure of the AFM superexchange interactions has been estimated by chemists to have the form shown below, and although the Hilbert space which describes the spin degrees of freedom has dimension 10^8 ($4^4 \times 8^5$), nevertheless one can use Lanczos exact diagonalisation techniques to try and get the lowest few hundred levels.

BELOW : STRUCTURE OF AFM COUPLINGS IN Mn-12
RIGHT : LOWEST STATES OF $\mathcal{H}_{eff}$ IN (58) & (59).





To get these exact diagonalisation results one needs to make some simple assumptions. These results were actually produced by making the ansatz. One starts by noting that the chemists estimates of the original superexchange couplings are



$$\left.\begin{aligned} J_1 &\sim 215\text{ K} \\ J_2 &\sim 85\text{ K} \\ J_3 &\sim 85\text{ K} \\ J_4 &\sim 45\text{ K} \end{aligned}\right\} \qquad (57)$$

Because J_1 is so strongly AFM, we make the assumption that the diagonal "spin pairs", linked by J_1 interactions, lock together into single spin-½ states (a kind of Mn^{3+}/Mn^{4+} dimer). The resulting system now has a Hilbert space of dimension 10^4. One can then write a model effective Hamiltonian, using the ansatz.

$$\mathcal{H}_{eff} = J_1 \sum_{\langle ij \rangle}^{4} \mathbf{S}_i \cdot \boldsymbol{\tau}_{j'} + J_2 \sum_{j'}^{4} \sigma_{j'} \cdot \sigma_{j'+1} + K_z \sum_{\langle ij \rangle}^{4} S_i^z \tau_j^z \qquad (58)$$

The constants J_1, J_2, and K_z are not calculated - they are instead fitted to data on $\chi_z(T)$ and $\chi_\perp(T)$. After this one has a model which can predict exptl data on any other kind of expt. One actually finds

$$J_1 = 85\text{ K} \qquad J_2 = -55\text{ K} \qquad K_z = 7.5\text{ K} \qquad (59)$$

Naturally a proper job on the spin structure of this model is more complex and difficult. Calculations using LDA methods can be used here; the Mn-12 system is just about at the limit of what can currently be done.

(a) Toy "Giant Spin" Model : From the discussion on the last page we see that many of these molecules have such strong AFM internal couplings, that it is reasonable to expect them to show a "Giant Spin" behaviour at low energies. By this we mean that the following truncation of the effective Hamiltonian can be carried out:

$$\mathcal{H}_{And} \rightarrow \mathcal{H}_0(\{s_j\}) \longrightarrow \mathcal{H}_0(\underline{S}_0) \qquad (60)$$

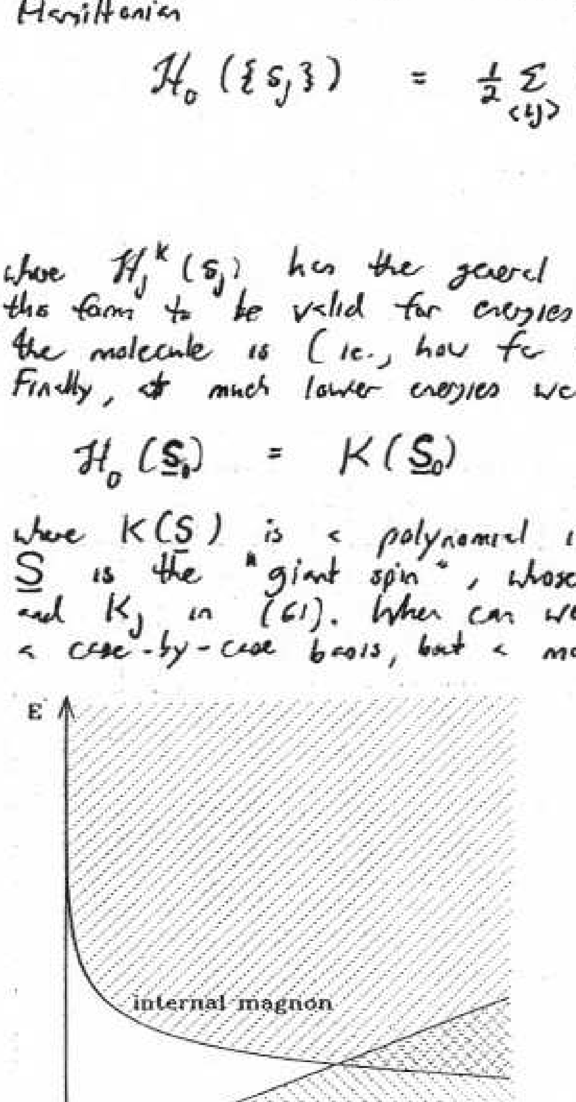
where one starts with an Anderson Hamiltonian like (1) for the system. Then truncates to a model in which phonons, photons, nuclear spins, and high-energy electron physics is dropped, leaving only the interacting electronic spins, with Hamiltonian

$$\left.\begin{aligned} \mathcal{H}_0(\{s_j\}) &= \frac{1}{2}\sum_{\langle ij\rangle} J_{ij}^{\alpha\beta} s_i^\alpha s_j^\beta + \text{higher exchange} \\ &\qquad + \sum_j \mathcal{H}_j^K(\underline{s}_j) \end{aligned}\right\} \quad (61)$$

where $\mathcal{H}_j^K(s_j)$ has the general spin anisotropy form given in (6). We expect this form to be valid for energies $\lesssim 1000K$, depending on how good an insulator the molecule is (ie., how far the Fermi energy is from any unfilled levels. Finally, at much lower energies we make the truncation to

$$\mathcal{H}_0(\underline{S}_0) = K(\underline{S}_0) \qquad (62)$$

where $K(\underline{S})$ is a polynomial in $\underline{S}$ of the same form as (6), but now $\underline{S}$ is the "giant spin", whose magnitude is governed by the different $J_{ij}^{\alpha\beta}$ and K_j in (61). When can we use (62). This has to be answered on a case-by-case basis, but a more general answer can be given by referring to the figure at left. The smallest possible system, a spin pair, will have a spin gap to higher excitations with a total $\underline{S} \neq \underline{S}_0$, with energy $E_G \sim J$. However if we now take a system with N_0 spins, and linear dimensions $L \sim a_0 N^{1/3}$, this gap will be rather less. We can distinguish 2 limiting cases, when $N_0 \gg 1$:



$$\text{FM limit :} \quad \left.\begin{aligned} S_0 &\sim N_0 \\ E_G &\sim \text{Max}\left[J N_0^{-1/3}, \hbar\omega_0^{FM}\right] \end{aligned}\right\} \quad (63)$$

$$\text{AFM limit :} \quad \left.\begin{aligned} S_0 &\sim O(N_0^{2/3}) \\ E_G &\sim \text{Max}\left[J N_0^{-1/3}, \hbar\omega_0^{AFM}\right] \\ |\underline{N}| &\sim O(N_0) \end{aligned}\right\} \quad (64)$$

where for very large N_0, E_G saturates at a lower bound of

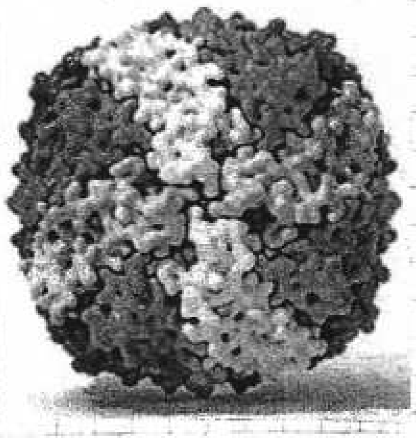
$$\left.\begin{array}{l} \hbar\omega_0^{FM} \sim K \\ \hbar\omega_0^{AFM} \sim (JK)^{1/2} \end{array}\right\} \qquad (65)$$

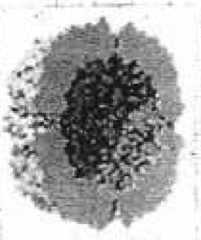
The explanation of the scaling in (63) & (64) is very simple. If the FM case, where almost all spins line up parallel, an internal "magnon" state with a flipped spin can form, in which the magnon delocalises around the molecule, thereby lowering its energy to $Ja_0/L \sim JN_0^{-1/3}$. For a very large molecule, the magnon energy is determined by the spin anisotropy. For the AFM case, where all couplings are AFM, there will still be a net moment from unpaired surface spins, whose number $\sim O(N^{2/3})$. Now an AFM magnon delocalizes, and the arguments go through as before.

These arguments are very crude but they work quite well for large molecules. Thus, eg., the "Ferritin" molecule, of molecular weight 480,000, has a core of ~ 4500 Fe^{3+} ions in an Fe_2O_3 hydrated crystalline form. This orders AFM, with a Neel moment $|\underline{N}| = 5/2\, g\mu_B N_0 \sim 22{,}500\ \mu_B$. From (64) we then expect the total moment to be

$$\left.\begin{array}{l} |S_0| \sim 2\mu_B N_0^{2/3} \\ \quad\ \sim 550\ \mu_B \end{array}\right\} \text{Ferritin} \qquad (66)$$

Ferritin protein consisting of 24 subunits





Cross section

THE FERRITIN MOLECULE (MW = 480,000) THE CENTRAL Fe_2O_3 CORE IS COVERED BY APOFERRITINS

and in fact $|S_0| = 614\ \mu_B$ in really well-prepared samples of Ferritin.

We thus see that for energies $E < E_G$, we can isolate the "giant spin" levels from all the higher excited states. This involves a huge Hilbert space truncation: If the original Hamiltonian $\mathcal{H}_0(\{S_j\})$ in (61) is made from spins with $|S_j| = S$, so there are $2S+1$ states per spin, then

$$\mathcal{D}\left[\mathcal{H}(\mathcal{H}_0(\{S_j\}))\right] = (2S+1)^{N_0} \qquad (67)$$

whereas the dimension of the Giant spin Hilbert space is

$$\left.\begin{array}{l} \mathcal{D}\left[\mathcal{H}(\mathcal{H}_0(\underline{S}_0))\right] \sim 2S_0+1 \\ \qquad\qquad\qquad\quad \sim O(N_0) \end{array}\right\} \qquad (68)$$

The range of energies over which $\mathcal{H}_0(\underline{S}_0)$ acts is governed entirely by the low-energy anisotropy fields acting on $\underline{S}_0$; we have a maximum energy

$$E_B \sim N_0 K \qquad (69)$$

This can also be understood in a very simple chemical way. If we rotate $\underline{S}_0$ (or $\underline{N}$) away from an easy axis or easy plane, then each spin $\underline{S}_j$ will have its energy raised by $\sim K$. The spins are locked together, so we get (69).

To get a better appreciation of this, lets consider an example - we take the case of the well-known Fe-8 molecule (page 14). This system is is known to be well-described by a giant spin Hamiltonian of form

$$\left.\begin{aligned}\mathcal{H}_0 &= -DS_z^2 + ES_x^2 + k_4^{\perp}(S_+^4 + S_-^4) + O(S^6) \\ &\equiv -\frac{K_2^z}{S}S_z^2 + \frac{K_2^{\perp}}{S}S_x^2 + \frac{K_4^{\perp}}{S^3}(S_+^4+S_-^4) + \cdots\end{aligned}\right\} \text{Fe-8} \qquad (70)$$

The values of the anisotropy constants cannot be calculated. Instead they are determined by experiment. Two sets of values used in the literature are

$$\left.\begin{array}{lll} D = 0.246\ \text{K} & \qquad & K_2^z = 2.46\ \text{K} \\ E = 0.092\ \text{K} & & K_2^{\perp} = 0.92\ \text{K} \\ k_4^{\perp} = 4.3\times10^{-6}\ \text{K} & & K_4^{\perp} = 4.3\times10^{-3}\ \text{K}\end{array}\right\} \begin{array}{l}\text{Neutron \&} \\ \text{ESR mmts}\end{array} \qquad (71)$$

$$\left.\begin{array}{lll} D = 0.230\ \text{K} & \qquad & K_2^z = 2.30\ \text{K} \\ E = 0.094\ \text{K} & & K_2^{\perp} = 0.94\ \text{K} \\ k_4^{\perp} = 3.28\times10^{-5}\ \text{K} & & K_4^{\perp} = 0.0328\ \text{K}\end{array}\right\} \begin{array}{l}\text{Mmts of} \\ \Delta_{10}^{10}(H_{\perp})\end{array} \qquad (72)$$

and these numbers illustrate first, how the results are uncertain, and second, how the potential is very accurately quadratic biaxial - the 4th-order terms are rather small.

Let us consider the spectrum of this system. The dominant term is the easy axis term, and the effect of this term is very simple. If we write

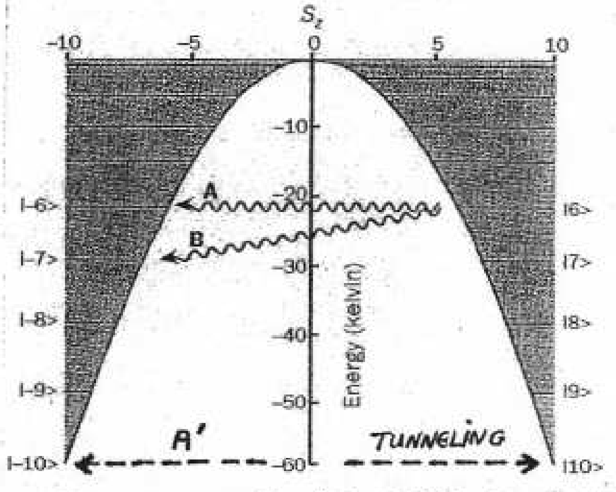
$$\mathcal{H}_0 = \mathcal{H}_0^{\parallel}(S_z) + \mathcal{H}_0^{\perp}(S_+, S_-)\ ; \qquad \mathcal{H}_0^{\parallel} = -DS_z^2 \qquad (73)$$

Then

$$\mathcal{H}_0^{\parallel}|S,M\rangle = -DM^2|SM\rangle \qquad (M = 0, \pm1, \pm2, \ldots \pm10) \qquad (74)$$

ie, we have an inverted parabola of states. Now suppose we add in the smaller transverse term, and do perturbation theory in the dimensionless parameter E/D. It is a useful exercise to then derive the following result for the splitting Δ_{10} that this term causes between the ground state degenerate pair of levels with $M = \pm 10$ in (74):

$$\left.\begin{aligned}\Delta_{10}^{10} &= A_S^S\, D\left(\frac{E}{4D}\right)^{S-1} \qquad (S=10) \\ \text{where} \quad A_S^S &= \frac{1}{2^{2S-2}}\frac{(2S)!}{[(S-1)!]^2}\end{aligned}\right\} \qquad (75)$$



ELASTIC TUNNELING (PROCESSES A & A') & INELASTIC TUNNELING (PROCESS B).

We see from this expression that for large S, the "tunneling amplitude" Δ_S^S through the large barrier created by $\mathcal{H}_0^{\parallel}(S_z)$ is a very rapid function of E/D when $E/D \ll 1$. Note that even if $E = 0$, the 4-th order term in (70) will also cause tunneling - one can fairly easily show that this would give a contribution

$$\left.\begin{aligned} \Delta_{10}^{10} &= A_5^S\, k_4^{\perp} \left(\frac{k_4^{\perp}}{D}\right)^{S/2-1} \\ A_5^S &= \frac{S^2}{2^S} \cdot \frac{(2S)!}{(S!!)^2} \end{aligned}\right\} \quad \begin{gathered} k_4^{\perp} \text{ contribution} \\ (S=10) \end{gathered} \qquad (76)$$

Moreover, even in the absence of any transverse terms, one can derive an expression for the splitting of the degenerate levels $|M\rangle, |-M\rangle$ by a transverse field – this we give here for general S & M:

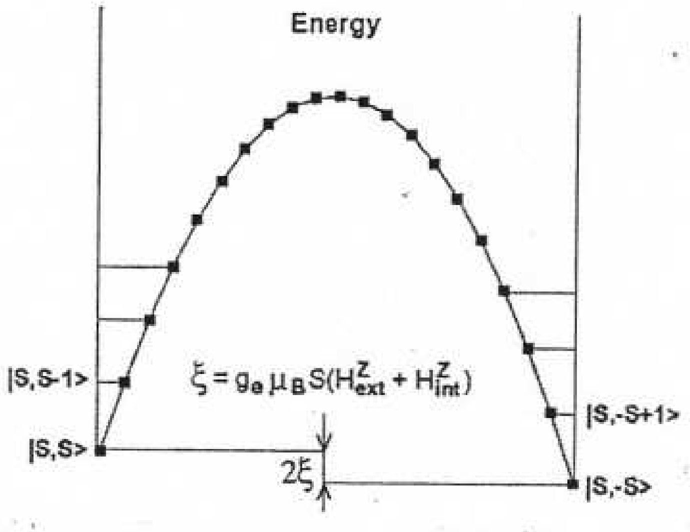
$$\text{If} \quad \mathcal{H}_0 = -D\hat{S}_z^2 - g\mu_B H_0^{\perp} \hat{S}_x \qquad (77)$$

$$\text{then} \quad \left.\begin{aligned} \Delta_M^S &= A_M^S\, D\left(h_0/2D\right)^{2M} \\ A_S^M(h_0) &= \frac{2}{[(2M-1)!]^2} \frac{(S+M)!}{(S-M)!} \end{aligned}\right\} \quad h_0 = g\mu_B H_0^{\perp} \qquad (78)$$

The structure of these expressions is very simple to understand. Given an operator like $h_0 S_x = \frac{1}{2}h_0(S_+ + S_-)$, we see that a "tunneling transition" occurs in perturbation theory via a sequence of perturbative "hops" from one side of the barrier to the other, one level at a time – thus we end up with an expression $\sim (h_0/D)^{2M}$ for a transition involving $2M$ hops, with energy denominator $\sim O(D)$. On the other hand if the transition is being accomplished by an operator like $(S_+^4 + S_-^4)$, then we have only $M/2$ hops; moreover, such an operator can only connect states differing in M by $4n$, where n is an integer.

Note one consequence of this – even if a high-order term is quite small, it may nevertheless make an important contribution to a perturbative expansion, simply because it is raised to a lower power.

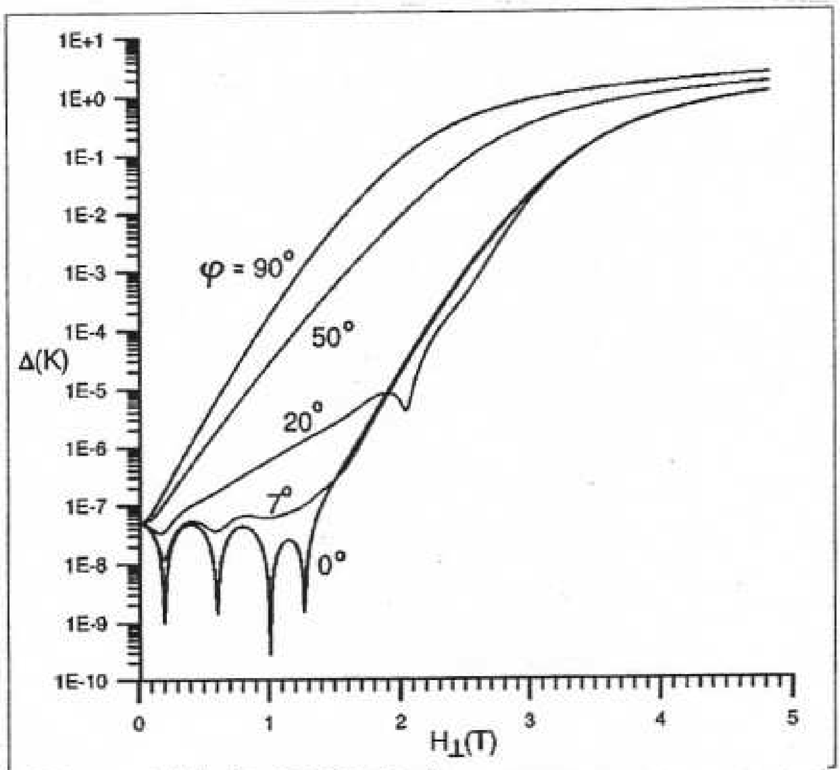
We notice also another consequence, which is essentially the revelation in the perturbation expansion of Kramers's theorem. If T-reversal symmetry is obeyed, then all the terms in $\mathcal{H}_0(S)$ will be even powers of components of $\underline{S}$. It then follows that $\Delta_S^S \neq 0$ only if S = integer. If S is half-integer then none of the operators in $\mathcal{H}_0(\underline{S})$ can connect $|S,S\rangle$ with $|S,-S\rangle$.



The effect of a longitudinal field is fairly straightforward – it simply "tilts" the potential. In any real system the total longitudinal field will be the sum of external fields, plus internal fields, from the other molecules, from nuclear spins, etc. The result of this is to cause a net "longitudinal bias" on the system, given by

$$\left.\begin{aligned} \xi &= \epsilon + \xi_{int.} \\ &= g\mu_B S\,(H_0^z + H_{int}^z) \end{aligned}\right\} \qquad (79)$$

acting to split the 2 lowest levels.



THE TUNNELING SPLITTING Δ_{10} FOR A SPIN-10 SYSTEM Fe-8, IN A TRANSVERSE FIELD AT AZIMUTHAL ANGLE φ WITH RESPECT TO THE X-AXIS.

How good are the perturbative results for the level structure of the system? One should always be suspicious of any perturbative expansion, and it is very easy to verify by numerically diagonalizing the Hamiltonian of a system like Fe-8 that there is a very interesting structure in the levels, as a function of transverse field, that is completely missed in the perturbative expansions like (75) or (78). The best way to understand this is using path integral methods, and we address this point below, when we discuss the spin dynamics of a central spin

Finally, we note that we can write a very simple effective Hamiltonian for the giant spin if we are able to make the final truncation to the 2 lowest levels. We then have

$$\left.\begin{aligned} \mathcal{H}_0(\hat{\underline{S}}_0) &\longrightarrow \mathcal{H}_0(\hat{\underline{\tau}}) \\ \mathcal{H}_0(\underline{\tau}) &= \Delta(\underline{H}_0^{\perp})\,\hat{\tau}_x + \epsilon(H_0^z)\,\hat{\underline{\tau}}_z \end{aligned}\right\} \quad (80)$$

where $\underline{\tau}$ is a Pauli matrix operating in the Hilbert space of the 2 lowest states. Clearly we can do this if we work at an energy scale ≪ the separation to the next states.

(b) Refinements to the Giant Spin Model.

There are 2 kinds of refinement one can make to the simple GS model. One is internal - including other interactions (eg., spin-orbit coupling, Dzyaloshinskii - Moriya interactions, etc) in a "proper way", as well as more detailed consideration of the internal electronic structure. These refinements are best considered theoretically using methods like LDF theory, and they properly capture the role of, eg., Jahn-Teller distortions to the inter-ionic bonds, and allow one at least in principle to derive the GS model in an ab initio calculation. In practise this is still very hard because of the enormous Hilbert space involved, so that so far it is quite hard to go beyond the kind of simple calculation presented above for Mn-12 (see p. 17).

The 2nd kind of refinement concerns the interaction of the GS with the rest of the world. In practise it may not always be obvious what the "rest of the world" is, but we can discern the following important interactions:

(i) <u>Substrate / Background Matrix</u> : One can imagine many possibilities here – the single molecule can be attached to chains, surfaces, and/or embedded in some 3-d matrix (which might itself be organised into chains or planes). Although theoretical study of these possibilities has hardly begun, the main lines of a theoretical approach are fairly clear – one has again to begin with an Anderson model of the kind we have already discussed.

The difficulty is that if we bring a molecule into contact with the substrate or embedding matrix, then through purely chemical effects (ie, involving the underlying energetics of the system, which determine the underlying structure of the molecule itself), the structure of the molecule will itself change. To understand such problems is completely beyond the scope of this course.

(ii) <u>Coupling to "Loose Spins"</u>: So far we have dealt with situations in which a central core strongly-coupled spins act together as a single "Giant spin". However one can certainly have situations in which other microscopic electronic spins are less strongly coupled to the central core, so that the truncation outlined in (60) does not work. Thus we can have a situation where a Hamiltonian of form

$$\mathcal{H}_0(\{S_j\}) = \frac{1}{2}\sum_{i,j\neq k} J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta + \sum_{j\neq k} \mathcal{H}_j^K(\underline{S}_j) + \cdots$$
$$+ \sum_{j\neq k} J_{jk}^{\alpha\beta} S_j^\alpha S_k^\beta + \mathcal{H}_k^K(\underline{S}_k) + \text{higher-order} \ldots \quad (8$$

where

$$|J_{jk}| \ll |J_{ij}| \quad (8$$

How we deal with the k-th "loose" spin depends on how big the J_{jk} are compared to other key energy scales. We can distinguish 3 cases:

- $|J_{jk}| > E_B$ where E_B is the energy barrier defined in eqtn (69). In this case, the loose spin is still sufficiently strongly coupled to $\underline{S}_0$ that we can include it with the giant spin.

- $E_B \gg |J_{jk}| > K$ In this case the levels of the giant spin mix with those of $\underline{S}_k$. However the giant spin itself will be left intact unless $|J_{jk}| \sim E_B$, and we can write an approximate Hamiltonian

$$\mathcal{H} \sim \mathcal{H}_{S_0}(S_0) + \mathcal{H}_K(\underline{S}_k) + \hat{\tilde{J}}_{\alpha\beta} S_0^\alpha S_k^\beta \quad (83)$$

where the coupling $\hat{\tilde{J}}_{\alpha\beta}$ will be related to the original coupling J_{jk}, but not in a simple way.

- $K \gg |J_{jk}|$ In this case we can safely accomplish the truncation to the qubit Hamiltonian in (80). There will be a residual coupling between the qubit $\underline{\tau}$ and the loose spin S_k, which we write in the form

$$\mathcal{H}_{int}(\underline{\tau}, S_k) = \lambda_k^{\alpha\beta} \tau^\alpha S_k^\beta \tag{84}$$

where again the coupling $\lambda_k^{\alpha\beta}$ can be related to the original couplings J_{jk}, but not in a simple way.

(III) Coupling to Nuclear Spins: In most cases we can assume that not only do the hyperfine couplings A_{jk} satisfy

$$|J_{ij}| \gg |A_{jk}| \tag{85}$$

but that they also satisfy $K \gg |A_{jk}|$ (86)

Thus, not only can we write that effective Giant Spin/Nuclear spin Hamiltonian, in the form

$$\left.\begin{aligned} \mathcal{H}^{int}_{Hyp}(S_0, \{I_k\}) &= \sum_k \tilde{A}_k^{\alpha\beta} S_0^\alpha I_k^\beta \\ \text{where the } \tilde{A}_k^{\alpha\beta} \text{ are roughly} \quad \tilde{A}_k^{\alpha\beta} &\sim \sum_j A_{jk}^{\alpha\beta} S_j^\alpha \end{aligned}\right\} \tag{87}$$

but we can also write an effective qubit/nuclear spin interaction in the form

$$\mathcal{H}^{int}_{Hyp}(\underline{\tau}, \{I_k\}) = \sum_k \omega_k^{\alpha\beta} \tau^\alpha I_k^\beta \tag{88}$$

The size of these couplings turns out to be of considerable interest, & will be discussed in more detail below; we have approximately that

$$|\omega_k^{\alpha\beta}| \sim O(|\underline{S}_0| \tilde{A}_k^{\alpha\beta}). \tag{89}$$

We see physically why we can make this truncation - if (86) is satisfied, then the hyperfine coupling cannot mix different giant spin levels separated by energies $\gtrsim K$. We will study the structure introduced in pairs of resonant qubit levels, or giant spin levels, once we have more formal tools.

(IV) Coupling to Phonons: The coupling of the giant spin to the phonons can be dealt with similarly to the coupling of a single spin. Thus we have a coupling of form

$$\mathcal{H}^{ph}_{int}(\underline{S}_0, \{b_{q\lambda}\}) = i \sum_{q\lambda} \underline{q} \cdot [g_q(\underline{S}_0) b_{q\lambda} - H.c.] \tag{90}$$

(cf. eqn. (15)), and the qubit-phonon coupling can be written as

$$\mathcal{H}^{ph}_{int}(\underline{\tau}, \{b_{q\lambda}\}) = \sum_{q\lambda} (V^\alpha_{\underline{q}\lambda} \hat{\tau}_\alpha b_{\underline{q}\lambda} - H.c.) \tag{91}$$

where the couplings $V_{\underline{q}\lambda}$ are of order $\quad |V^{\alpha}_{\underline{q}\lambda}| \sim O\,(|\underline{S}_0| g_{\underline{q}})$. $\quad$ (92)

That we can truncate the spin-phonon couplings in this way is not completely obvious, simply because phonons can have rather high energy - there is no reason to suppose we cannot have appreciable matrix elements of phonons between different giant spin levels, or even transitions between different individual electronic spin levels which take the system outside the giant spin subspace entirely.

This is a real problem, and in fact one can attribute structural distortions of the molecule to the effect of spin-phonon couplings. It is actually surprising how weak the effects often are; the explanation lies in the strength of the spin-phonons couplings, since

$$|g_{\underline{q}}(S_0)| \sim O\,(K) \tag{93}$$

This means that transitions involving high-energy phonons of energy $\omega_{\underline{q}}$ have an effect on low-energy physics $\sim |g_{\underline{q}}|^2/\omega_{\underline{q}}$ (for energy shifts), which is rather small in most cases. Nevertheless spin-phonon mediated transitions play a crucial role in all the physics, since they allow the spin system to come to equilibrium with the phonon bath (in the same way that hyperfine interactions allow the electronic system to equilibrate with the spin bath). At low T, almost all of the entropy of the system will be in local degrees of freedom (electronic spins, nuclear spins) but only the phonon bath can communicate efficiently with the outside world.

(V) <u>Coupling to Photons</u> : This has the form that one might expect, ie., we have a photon / giant spin coupling of form

$$\left.\begin{aligned} \mathcal{H}^{int}_{A}(\underline{S}_0, \{a_{\underline{q}s}\}) &= 2\mu_B\, \hat{\underline{S}}_0 \cdot \hat{\underline{B}}(\underline{r},t) \\ \hat{\underline{B}}(\underline{r},t) &= \frac{i}{\sqrt{V}} \sum_{\underline{q}s} \left(\frac{\hbar}{2\varepsilon_0 \omega_{\underline{q}}}\right)^{1/2} \left[a_{\underline{q}s} (\underline{q} \times \underline{\varepsilon}_{\underline{q}s}) - H.c. \right] \end{aligned}\right\} \tag{94}$$

where we assume for simplicity that the g-factor of the giant spin is isotropic and equal to 2. The resulting photon-qubit coupling has the form

$$\mathcal{H}^{int}_{A}(\hat{\underline{\tau}}, \{a_{\underline{q}s}\}) = \sum_{\underline{q}\lambda} \left(c^{\alpha}_{\underline{q}s}\, \hat{\tau}_{\alpha}\, a_{\underline{q}s} - H.c. \right) \tag{95}$$

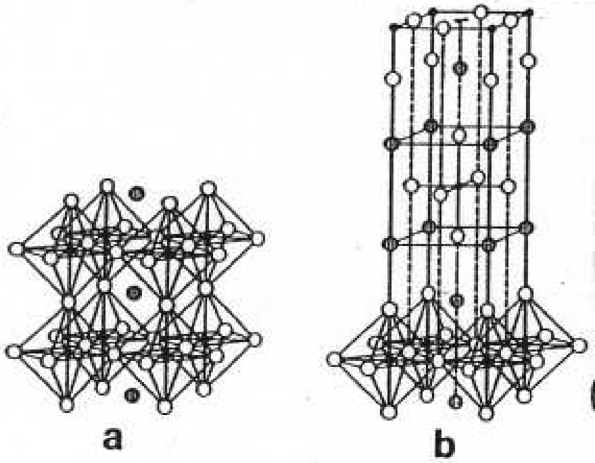
Again, the effect of photons is small because the effective couplings are small. The most important role of photons is actually experimental - the energy of transitions between the GS levels, of order $K \sim 1$-$10\,K$, corresponds to μwaves, and so these systems can be examined using μwave or ESR measurements in some detail.

Note that there are other interactions we might have considered here. These include interactions between electric dipoles inside the molecules and the electric field, as well as interactions with other experimental probes like neutrons. The electric interactions allow the system to interact with electric dipoles outside the system, so that in principle our magnetic giant spin can interact with electric dipole defects in its surroundings. Such defects are universally present in solid-state systems, as we shall discuss when we come to the subject of glasses.

A.1.3 CONDUCTING NANOMAGNETS

In the same way that we can plant insulating magnetic "nanocores" into a ligand shell, to produce nanomagnetic insulating molecules, one can also make conducting magnetic nanocores, which can also be surrounded by ligand shells. As with magnetic molecules, the outer ligand shells play a crucial role, - although it is slightly different here. To see how things work it is useful to first survey some of the different systems, and then give a brief sketch of how they are modelled, and what theory says about this.

(a) The Physics of "Metallic Clusters" : We are actually dealing with a huge field here, which touches not only upon a broad area of nanoscience, but also on a large variety of interesting materials which have interesting strong electron-electron correlations, including those which lead to high-temperature superconductivity. To see this we begin with some systems where the nanocores are very small. These include some systems that are very well known to physicists working in superconductivity and/or quantum magnetism. The cubic perovskite systems, and similar perovskites with, eg., tetragonal symmetry, give a large variety of systems which include the high-T_c cuprate superconductors. The layered K_2NiF_4 structure is named after a well-known quantum magnet. In both cases a small group of metallic ions, with spin, is enclosed in a ligand cage (labelled by M and L in the figure at left).



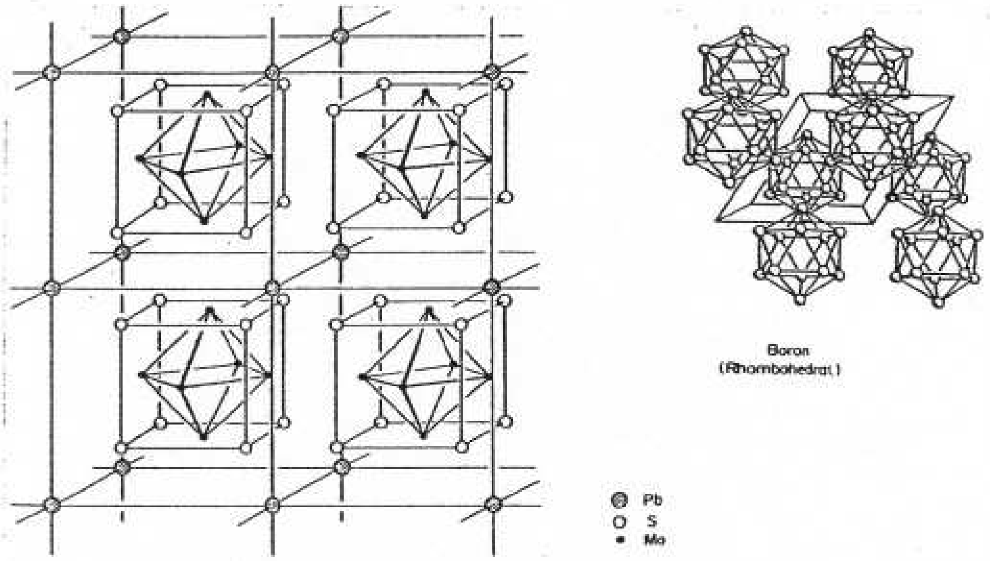
CLUSTERS OF THE FORM ML_6 (WHERE M = METAL, L = LIGAND).
(a) THE CUBIC PEROVSKITE STRUCTURE
(b) THE K_2NiF_4 STRUCTURE

The importance of the ligand groups now appears - there are basically 3 main points here:

(i) The ligands stabilize a particular core structure

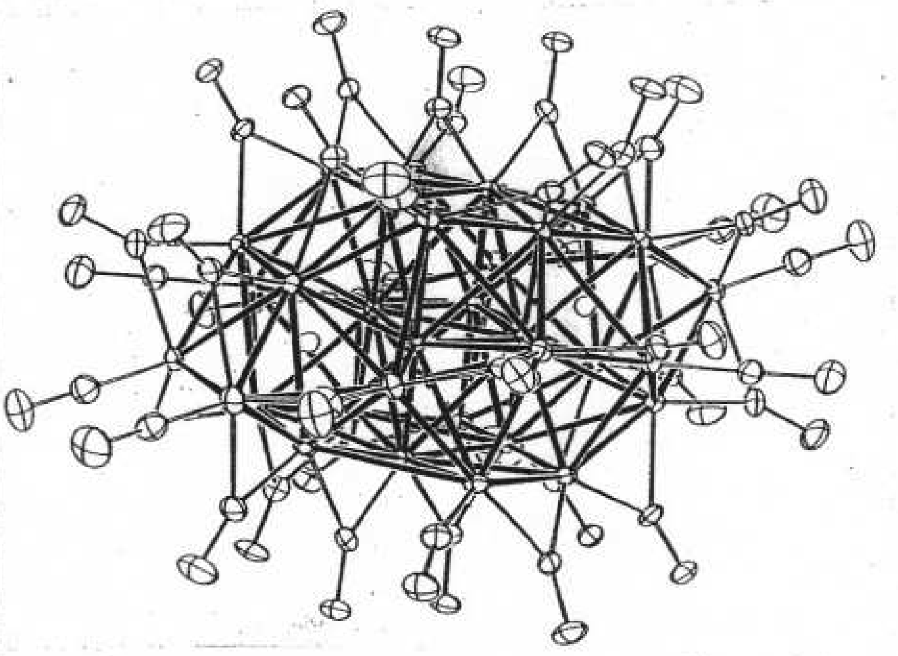
(ii) The ligands can link together, to give a variety of 1-d, 2-d, or 3-d structures incorporating the metallic cores in a regular way (eg, a chain, or a 3-d crystal lattice).

(iii) Without the ligands, the metallic ions find it hard to form any given structure - instead, they prefer to amalgamate into irregular, even amorphous "globs", or other ill-defined structures; this happens when d = 1, 2, or 3.



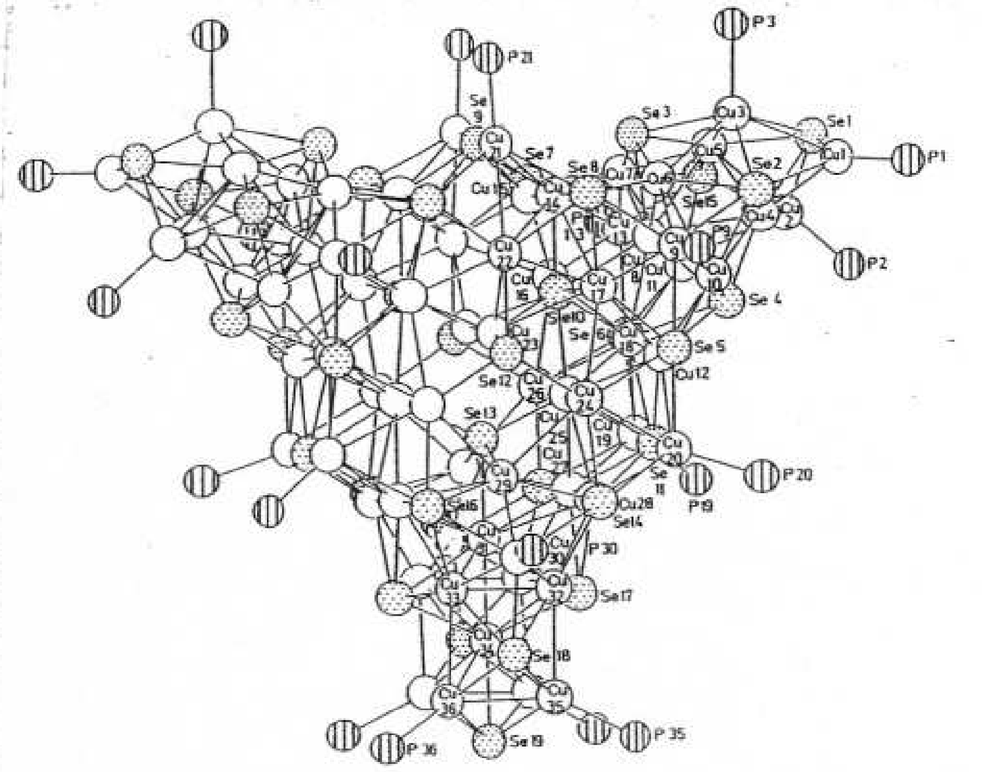
Left: MO_6L_8 metal-cluster molecules found in the Chevrel phases (e.g. $PbMO_6S_8$).
Right: Icosahedral B_{12} clusters froming the rhombohedral structure of boron.

The interesting thing is quite how large one can make the nanocores of these systems. Many hundreds of compounds have now been prepared & explored with very large metallic central units. Not all of these can be made in crystalline arrays, but here we show some examples which can be made in 3-d crystalline form, and which are well characterised. In these systems, a very large core of TM-base spins is created (the so-calle "metallic cluster"). The ions are themselves nearly always magnetic, but the internal spin structure depends very much on the geometry, and on the way in which the electron-elec interactions translate, in a condu into a low-T correlated state.



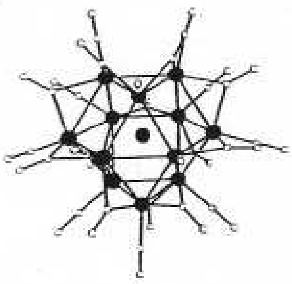
Structure of the metal cluster molecule $[Ni_{34}(CO)_{38}C_4H]^{5-}$

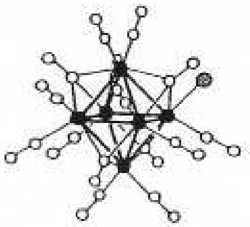
The systems shown here are not the largest of these metal cluster systems, that can be made in crystalline arrays. Thus, eg., the compound $Cu_{70}Se_{35}(PEt_3)_{22}$, or else $Cu_{70}Se_{35}(PEt_2Ph)_{23}$, shown below, are not the largest of this class of "Cu_2Se" systems - this honour is held at present by the $Cu_{146}Se_{73}(PPh_3)_{30}$ system. Note they can also make Cu_2Se in bulk (without all the ligands), in crystalline form - it is actually a semi-metal with a high conductivity. Many of these large cluster systems have interesting magnetic properties, in the same way as their insulating counterparts - they are often referred to as "magnetic chemical nanostructures", which means that they are nanosystems constructed using a "bottom up" chemical approach (as opposed to a "top down" physical approach (the latter involving techniques like molecular beams, lithography, STM's, etc).

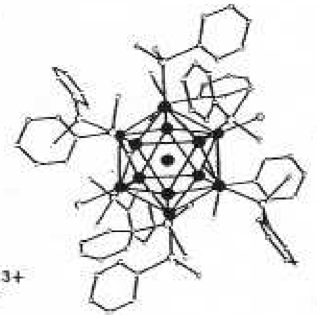


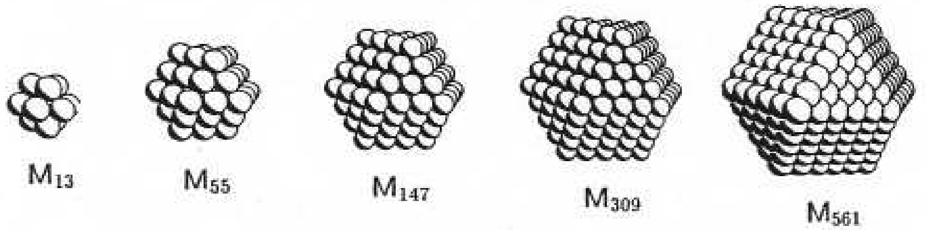
Structure of the cluster molecule $[Cu_{70}Se_{35}(PEt_2Ph)_{23}]$. (C-atoms are not shown).

Study of these systems is still in its infancy - exploration of crystalline arrays made from very sub-units such as the perovskite or the Chevrel structures shown on the last page have already shown what a remarkable variety of exotic many-body effects can appear. The enormous variety of ligand groups available to put the nanocore clusters into various structures means that this field will continue to develop for a long time to come - examples of such ligands include very simple groups, such as non-metallic atoms like O, or a halide (these being common in simple TM compounds like perovskite superconductors or NiO, etc), or they can be simple molecules like H_2O or CO (as in the large group of carbonyl clusters), or more complex molecules like acetate groups, pyridine, pyrazol, phosphine, etc. The final system may be neutral, and then groups can bind to form structures analogous to molecular solids - or they can be charged, and combine with suitable counterions to form ionic compounds or structures.


$[Rh_{13}(CO)_{24}H_{5-n}]^{n-}$


$[Rh_6(CO)_{15}I]^-$


$[Au_{13}(PPhMe_2)_{10}Cl_2]^{3+}$

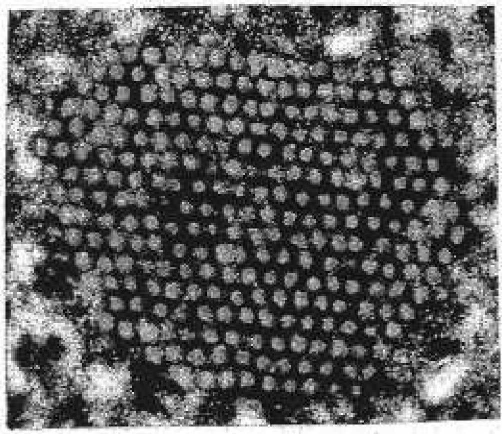


Magic-number clusters M_n obtained by surrounding a given atom by successive shells of atoms (the illustration is for cuboctahedral packing).

We note that the internal structure of a metallic core will be determined by many factors as well; since the system is metallic, we have intimate coupling between the TM ions themselves (un-mediated by any intermediate non-metallic ions) and this can determine interesting ordered structures inside the core itself. Examples are shown above, both at the very small scale, and for much larger "magic number" clusters. These have been made very large - for example, magic number clusters of Pd have been made up to $Pd_{2057}\,Phen_{78}\,O_{1600}$. In these systems, the ligands are only on the outside, and the core is purely metallic. The metals used so far include Co, Pd, Au, Pt, Ru, and Rh, and the ligands include PPh_3, PMe_3, $P(t\text{-}Bu)_3$, $As(t\text{-}Bu)_3$, and $P(p\text{-}tolyl)_3$.

Finally, one can imagine stripping away the ligand groups entirely, and working purely with conducting magnetic nanoparticles. Obviously it is much more difficult to control the size & shape of such particles - this is the weakness of top-down approaches. Nevertheless the physics of such systems has been of some interest to people working in mesoscopic physics and nanoelectronics. They can also be coupled to conducting or insulating matrices

While a detailed understanding of these systems is clearly going to be complicated, we will see that in many respects they are quite simply related to the smaller conducting systems we studied above. Conducting magnetic particles, both mesoscopic & nanoscopic, have actually been around for a long time. They are formed in many natural processes (eg., spark discharges), and used in, eg., magnetic recording tapes where they store information in their polarisation.

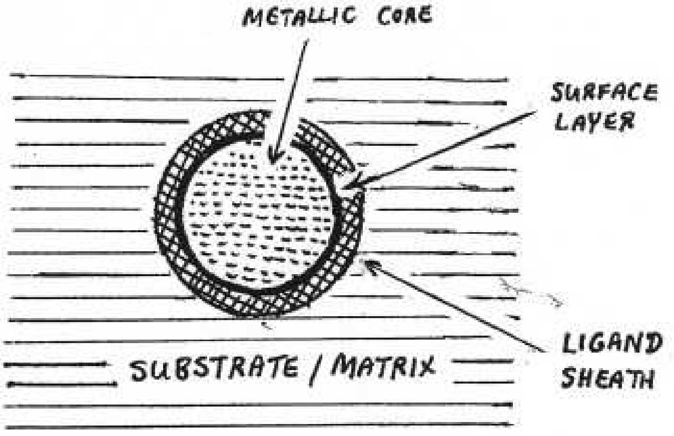


A Ni CLUSTER ON AN UNDERLYING Si SUBSTRATE

(b) Simple Models for Metallic Clusters

: One can set up a rather simple description of metallic clusters, without going into the complex details of an effective Anderson model for the system (this model including the detailed description of each ion in the cluster, the ligands, and any other relevant ion in the background matrix or substrate).

To give a simple approximate description of the system we make the division shown in the diagram. We imagine that the outermost metallic layer of the core is strongly distorted by the ligands which attach to it - this is something which can be verified experimentally. This single layer separates the metallic nanocore proper from the ligands. Finally we have the outer substrate or 3-d matrix.



This model is of course a simple caricature of the physics, but it is quite useful in analysing the magnetic and electrical coupling between the core and the outside world. We then model the individual components as follows:

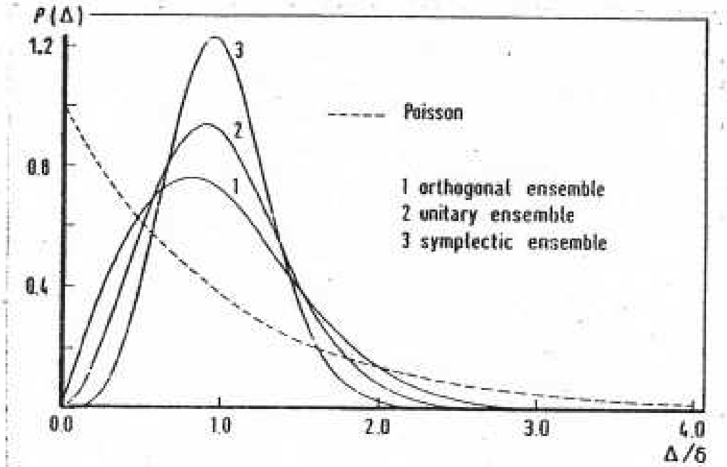
(i) Metallic Core : In the usual way we can model the core as a finite Anderson lattice model, which may or may not be periodic. Since typically we are interested only in the properties near the Fermi energy, and the system is assumed to be metallic, we can also approximate this by a FM or an AFM - ordered Fermi liquid, with effective Hamiltonian

$$\mathcal{H}_{eff}^{CORE} = \sum_{\mu\sigma} E^{0}_{\mu\sigma}\, \delta n_{\mu\sigma} + \frac{1}{2} \sum_{\substack{\mu\sigma \\ \nu\sigma'}} f_{\mu\nu}^{\sigma\sigma'}\, \delta n_{\mu\sigma}\, \delta n_{\nu\sigma'} \qquad (96)$$

where we assume to be definite a FM - ordered system with a total moment

$$M = \sum_{\mu\sigma} \sigma\, \delta n_{\mu\sigma} \qquad (97)$$

The key point here is the set of discrete (but extended) states $|\mu\sigma\rangle$; these are confined to be inside the nanocore. One can easily give the exact distribution of these states, if we know the exact shape of the core - failing this, one can simply assume a distribution of levels with a corresponding distribution $P(\Delta)$ of energy separations Δ between adjacent levels. It is common in the theory of mesoscopic or nanoscopic systems to analyze an ensemble of these systems using "random matrix" theory, which have a characteristic form for $P(\Delta)$, depending on the underlying symmetries of the system concerned - see Fig. at left. There are however 2 reasons why one



needs to treat these theories with caution. The first is that the nanocores are not really random systems – they are built from atoms whose states are not randomly distributed, and they are organised in structures which are typically not random either. The second point is that the properties of a given individual system, and of the spacing between a few levels near the Fermi energy, may be rather different from what one might infer from any of the distribution functions.

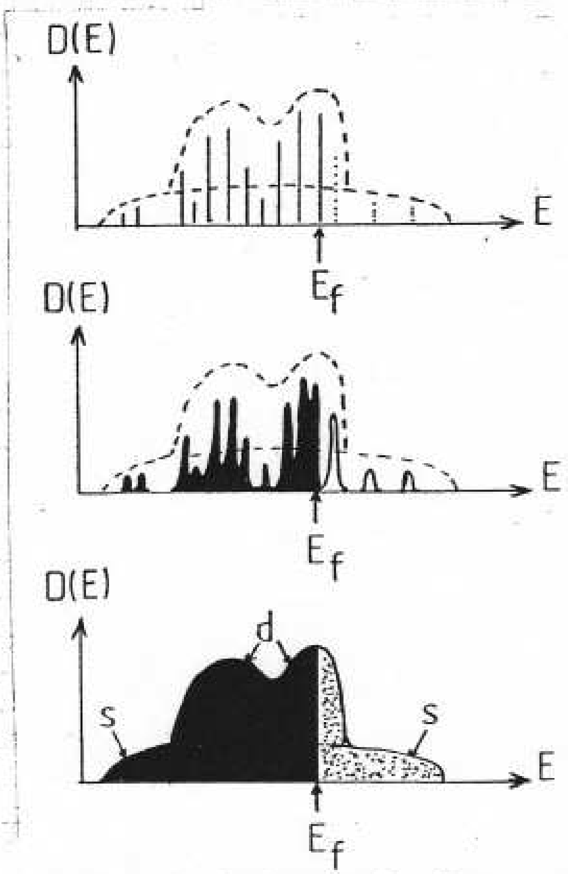
For a FM conducting particle, the average level splitting is

$$\bar{\Delta} \equiv \bar{N}_{\epsilon}^{-1} \sim W/N_0 \sim O(W/S_0) \qquad (98)$$

where we assume N_0 metallic ions, with a spin $\sim O(1)$ for each one.

(ii) Surface Layer: The surface sheath is the outermost layer of metallic ions in the nanocore. It has quite different properties from the rest of the nanocore, because the metallic ions in this layer are directly coupled to the ligands. The typical result of this is change the occupation of the TM-ion d-levels, often to fill them completely, thereby making these surface ions effectively insulating, and also changing the moment of the surface ions from their bulk values.

A typical example is provided by the large group of Ni-carbonyl clusters, which have been studied using DFT methods for clusters as large as $Ni_{44}(CO)_{48}$ as well with extensive experiments using local probes, in particular NMR. The moment of the Ni atoms in the interior is roughly $0.7\,\mu_B$ per atom – this is because the atomic configuration of $3d^9 4s^1$ is only weakly perturbed by the sd hybridisation, at the Fermi energy, which is found as shown in the figure. In both the bulk system and the nanocluster, the bonding between the Ni atoms is thus mediated mostly by the delocalised 4s electrons.



Sketch of the DOS as a function of energy for a d-metal cluster as compared to the bulk Top: discrete cluster orbitals. Middle: cluster orbitals each broadened by a Gaussian distribution. Bottom: bulk metal DOS. The Fermi energy E_F separates occupied and unoccupied levels in each plot.

In the surface layer things are quite different. The CO σ-bonds have repulsive interactions with Ni 4s-electrons, pushing the 4s electrons above ϵ_F. Thus the surface layer Ni ions have the configuration $3d_{10}$, via a charge transfer from the 4s levels. Another way to think of this is as a strong crystal field effect, in which the Ni moment is quenched by the strong crystal field from the CO orbitals, ie, the crystal field energy is stronger than the 4d Hund's rule coupling.

The net effect of this is to create an insulating barrier to any charge transport out of the system – electrons need to hop to a higher level in the surface layer, separated from ϵ_F by a charge transfer gap. The "tunneling amplitude" through this state is then

$$t_s \sim \frac{|V_{sB}|^2}{\Delta_{sB}} \qquad (99)$$

where V_{SB} is the hybridisation coupling, between the conduction electrons at the Fermi energy in the bulk, and the localised level in the surface layer at a charge transfer energy Δ_{SB} above the Fermi energy.

(iii) <u>Ligand Sheath</u>: Any electrons attempting to pass through the ligand sheath must also pass through levels removed from the Fermi energy by a charge transfer gap. It is hard to make any generalisations about this, because of the huge variety of ligand groups. In general one will have optimal conduction paths through the ligand groups to the outside world, and along with the surface layer, this will give us an effective tunneling Hamiltonian coupling the mobile electrons inside the metallic core, to the outside substrate or 3-d matrix. Thus we finally have the following 2 possibilities:

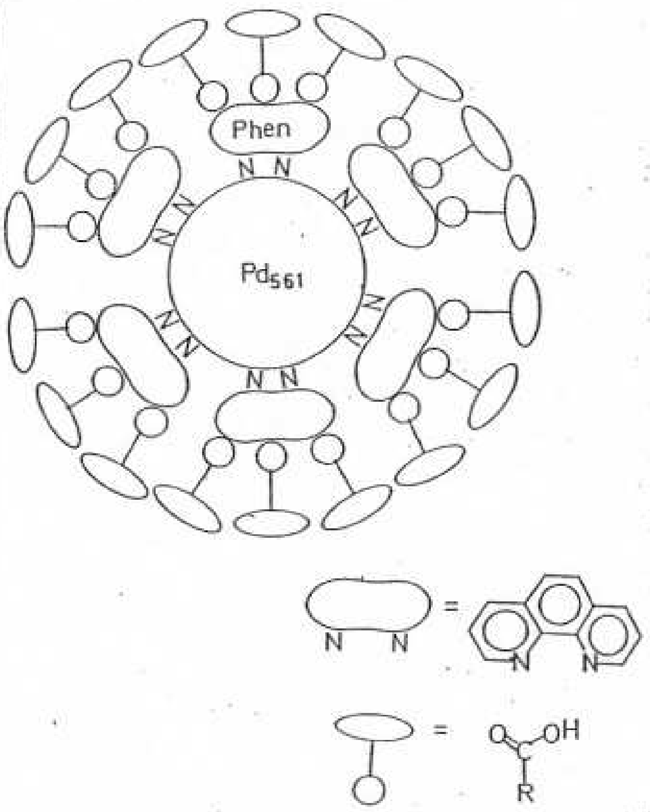
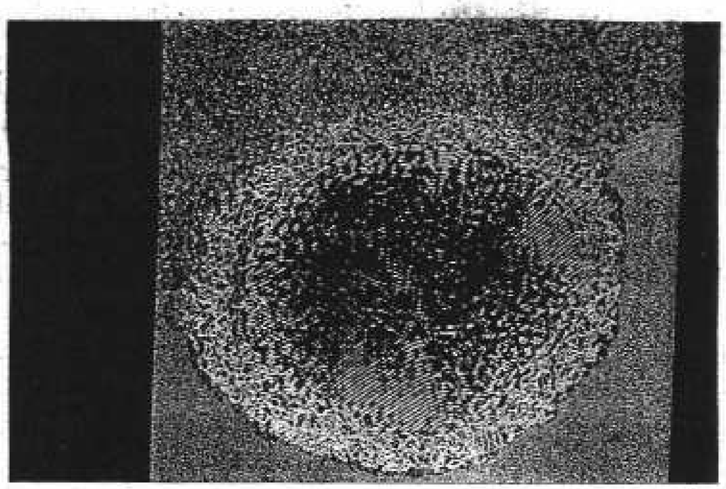


Illustration of the two ligand shells around a Pd_{561} cluster formed by hydrophobic-hydrophobic interaction.



HRTEM image of a single gold colloid with 13.2 × 10.5 nm. The polycrystalline structure as well as the ligand shell, consisting of $P(m\text{-}C_6H_4SO_3Na)_3$ molecules, can be observed.

- Insulating Substrate: In this case the electrons are confined to the inside of the nanocore, and we are left with the effective Hamiltonian given in (96).

- Conducting Substrate: The tunneling now couples mobile electrons between the core & the substrate, yielding a total Hamiltonian

$$\left.\begin{aligned} \mathcal{H}_{eff} &\sim \mathcal{H}_{eff}^{CORE} + \sum_{\mu \underline{k} \sigma} \left(t_{\mu \underline{k}} d^{+}_{\mu\sigma} c_{\underline{k}\sigma} + H.c. \right) + \mathcal{H}_{eff}^{SS} \\ \mathcal{H}_{eff}^{SS} &= \sum_{k\sigma} \epsilon_{k\sigma} c^{+}_{k\sigma} c_{k\sigma} \end{aligned}\right\} \quad (100)$$

where we ignore electron-electron interactions in the substrate. The tunneling matrix elements between the discrete states $|\mu\sigma\rangle$ inside the nanocore, and the continuum of states outside, will fall off rapidly with the thickness of the ligand sheath.

Note again the limitations & approximations which have led to the results summarized in (96), (97), and (100). We have dropped all reference to the original Anderson model which may lead to these forms, and we are simply left with the phenomenological forms given. These are only valid in a range near the Fermi energy, and they are only useful in systems which are far from a metal-insulator transition. This of course is entirely in the spirit of Fermi liquid theory.

It is possible to do a great deal with the theory employed here, in the study of nanoelectronic systems.

A.2. CENTRAL SPIN DYNAMICS

After the preceding rather extensive survey of the different kinds of effective Hamiltonian that can lead to a "Central Spin" model, we now come to the dynamics. In this section we will look at 4 things, viz.,

- How can one usefully calculate the spin dynamics of an isolated central spin, which is not even coupled to its surrounding environment? This is an interesting pedagogical problem, which allows us to take on board some useful techniques - notably the use of WKB and path integrals for spin

- In cases where the central spin is coupled to an oscillator bath, and where the system can be treated as a "giant spin", one deals with a spin-boson model, which in its most common form reduces to a low-T spin-½ coupled to an oscillator bath environment. We give details on the spin-boson dynamics.

- When the coupling of the central spin to the surrounding spin bath dominates, we deal with the dynamics of a central spin coupled to a spin bath - again, one is interested either in the full giant spin or the spin-½ qubit.

- Finally, it is very useful to look at a real example or two. This we do, by looking at both a simple rare earth system, and at a magnetic molecule.

Before beginning, let's summarize the models that we intend to study and what are the important parameters in them:

(i) **Bare "Giant Spin" Model** : This model is supposed to describe a single spin $\underline{S}_0$, which moves in some anisotropy field $K(S_0)$. The Hamiltonian in a magnetic field is

$$\mathcal{H}_0(\hat{\underline{S}}_0) = K(\hat{\underline{S}}_0) - \mu_B g_{\alpha\beta} S_0^{\alpha} H_0^{\beta} \qquad (101)$$

where $K(S_0)$ is an even polynomial in $\underline{S}$, of order S_0, and we assume the "giant spin" model for the system. If truncated to the lowest 2 levels, the system reduces to a "qubit" model:

$$\mathcal{H}_0(\hat{\underline{\tau}}) = \Delta(\underline{H}_0)\hat{\tau}_x + \epsilon(\underline{H}_0)\hat{\tau}_z \qquad (102)$$

where the dependence on $\underline{H}_0$ has to be calculated.

(ii) **Spin-Boson Model.** : Now we couple $\underline{S}_0$ to a set of oscillators, which may represent phonons, photons, or perhaps electrons. This means generalising (101) to the form

$$\mathcal{H}_{SB}(\underline{S}_0, \{b_q\}) = \mathcal{H}_0(\hat{\underline{S}}_0) + \sum_q \hbar\omega_q (b_q^{\dagger} b_q + \tfrac{1}{2}) + \sum_q V_q(\underline{S}_0)(b_q - b_q^{\dagger}) \qquad (103)$$

or similar couplings of this sort (for simplicity the possible polarisation indices, etc., have been suppressed here). Then, as we will discuss, one can at low energies discuss the qubit version of the spin-boson model:

$$\mathcal{H}_{SB}(\underline{\tau}, \{x_q\}) = \mathcal{H}_0(\hat{\underline{\tau}}) + \frac{1}{2}\sum_q \left(\frac{p_q^2}{m_q} + m_q^2\omega_q^2 x_q^2\right) + \sum_q C_q^{\alpha}\hat{\tau}_{\alpha}\, x_q \qquad (104)$$

where the $\{x_q, p_q\}$ are canonically conjugate coordinates for the oscillators; the connection between $V_q(\underline{S}_0)$ and the C_q^{α} is to be determined.

(iii) **Central Spin Model** : Now we couple $\underline{S}_0$ to a bath of spins or other discrete-state systems. The general kind of model we are interested has the form

$$\left.\begin{aligned} \mathcal{H}_{CS}(\underline{S}_0, \{\underline{I}_k\}) &= \mathcal{H}_0(\underline{S}_0) + \mathcal{H}_0(\{\underline{I}_k\}) + \sum_k \tilde{A}_k^{\alpha\beta} S_0^{\alpha} I_k^{\beta} \\ \text{where} \quad \mathcal{H}_0(\{\underline{I}_k\}) &= \sum_k \left(\underline{h}_k \cdot \underline{I}_k + Q_k^{\alpha\beta} I_k^{\alpha} I_k^{\beta}\right) + \sum_{kk'} V_{kk'}^{\alpha\beta} I_k^{\alpha} I_{k'}^{\beta} \end{aligned}\right\} \qquad (105)$$

where the $\{I_k\}$ can represent magnetic or other defects, paramagnetic impurities, or nuclear spins. In the qubit limit this reduces to

$$\mathcal{H}_{CS}(\underline{\tau}_0, \{\underline{I}_k\}) = \mathcal{H}_0(\hat{\underline{\tau}}) + \mathcal{H}_0(\{\underline{I}_k\}) + \sum_k \omega_k^{\alpha\beta}\hat{\tau}_{\alpha} I_k^{\beta} \qquad (106)$$

In what follows, we will often assume, to simplify things, that the spin bath degrees of freedom are TLS (Two-Level Systems).

A.2.1. GIANT SPIN DYNAMICS

In section A.1.2(a), eqtns (70)-(80), we gave some preliminary perturbative results for the transition matrix elements between states, using perturbation theory in the ratio of transverse fields to the dominant anisotropy term. This was done for a simple example.

In this section we extend this to a somewhat more general discussion of the spin dynamics, using a non-perturbative technique which is based on the use of spin path integrals.

(a) Spin Path Integral : A very nice way of doing non-perturbative analyses of quantum dynamics is provided by the path integral technique. Recall how this technique works - one starts from a classical Lagrangian for a given physical system, and then finds the transition amplitude between 2 quantum states by summing over all classical paths, in the classical generalised coordinate space, and then projecting onto the quantum states from the classical space. Thus, e.g., the amplitude to go between states $|\psi_{in}\rangle$ and $|\psi_{fin}\rangle$ for a system with classical Lagrangian $L(x,\dot{x};t)$ is given by

$$\left.\begin{aligned} K_{fi}(t_f,t_i) &\equiv \langle\psi_f|\hat{U}(t_f,t_i)|\psi_{in}\rangle \\ &= \int dq_1\int dq_2\,\langle\psi_f|q_2\rangle\,K(q_2,q_1;t_f,t_i)\,\langle q_1|\psi_{in}\rangle \end{aligned}\right\} \quad (107)$$

where

$$K(q_2 q_1;t_f,t_{in}) = \int_{x(t_i)=q_1}^{x(t_f)=q_2} \mathcal{D}x(t)\; e^{\frac{i}{\hbar}\int_{t_i}^{t_f}dt\,L(x,\dot{x};t)} \quad (108)$$

and, as usual, the notation $\int\mathcal{D}x(t)$ indicates a functional integral over all classical paths between the limits in the integral (in this case these limits are the coordinates q_1 at time t_{in}, and q_2 at time t_f).

The basic problem with setting up a path integral for spin is that there are no classical states for spin (recall that spin disappears in the limit $\hbar\to 0$). For any spin system with finite quantum number, all we have is a finite set of discrete states. A somewhat related problem is that we don't at the moment have a Lagrangian for a single spin.

The solution to this problem can be given in 2 steps, viz:

- Define the "classical states" by using the coherent states for spin that we have already seen.

- Assume that the Lagrangian has the same form as that for a classical angular momentum.

Thus the first step consists in writing, for the propagator between 2 spin states, the form

$$K_{fi}(t_f,t_{in}) = \int d\underline{n}_1\int d\underline{n}_2\,\langle\psi_f|\underline{n}_2\rangle\,K(\underline{n}_2,\underline{n}_1;t_f,t_{in})\,\langle\underline{n}_1|\psi_{in}\rangle \quad (109)$$

where we write symbolically

$$K(\underline{n}_2, \underline{n}_1 ; t_2, t_1) = \int_{\underline{\Omega}(t_1) = \underline{n}_1}^{\underline{\Omega}(t_2) = \underline{n}_2} \mathcal{D}\underline{\Omega}(t)\, e^{\frac{i}{\hbar}\int dt\, L(\underline{\Omega}, \dot{\underline{\Omega}} ; t)} \qquad (110)$$

We will look below at how (110) is to be interpreted.

The 2nd step is best understood by considering the classical eqtn. of motion for an angular momentum $\underline{L}$. This is just

$$\frac{d\underline{L}}{dt} = -\underline{L} \times \frac{\partial H}{\partial \underline{L}} \equiv -\underline{L} \times \underline{T} \qquad (111)$$

where $\underline{T}$ is the torque acting on $\underline{L}$. We note that the formal operator of eqtn of motion for $\underline{S}(t)$ in a quantum system obeys the same equation, and because

$$\underline{S} = \langle \underline{n} | \hat{\underline{S}} | \underline{n} \rangle \qquad (112)$$

we can verify that $\underline{n}(t)$ does too. Now consider the following Lagrangian:

$$L(\underline{n}, \dot{\underline{n}} ; t) = S\underline{A} \cdot \frac{d\underline{n}}{dt} - \mathcal{H}(S\underline{n}) \qquad (113)$$

where $\underline{A}$ is a fake gauge potential, due to a unit monopole at the centre of the Bloch sphere; this means that

$$\underline{n} \cdot (\underline{\nabla} \times \underline{A}) \equiv n_\alpha \epsilon^{\alpha\beta\gamma} \frac{\partial A_\beta}{\partial n^\gamma} = 1 \qquad (114)$$

The Lagrangian in (113) is now written in terms of an ordinary vector quantity $\underline{n}(t)$, which takes the role of the classical variable. Note that two commonly used forms for $\underline{A}$ are

$$\underline{A} = \left\{ \begin{array}{ll} -\hbar \hat{\phi} \cot\theta & (\text{Polar gauge}) \\ \hbar \hat{\phi} \dfrac{1-\cos\theta}{\sin\theta} = \dfrac{\hat{\underline{z}} \times \underline{n}}{1 + \hat{\underline{z}} \cdot \underline{n}} \hbar & (\text{Dirac gauge}) \end{array} \right\} \qquad (115)$$

This answers the formal question of how to write a spin path integral. We now need to say a few words about what expression (110) means, both formally and physically.

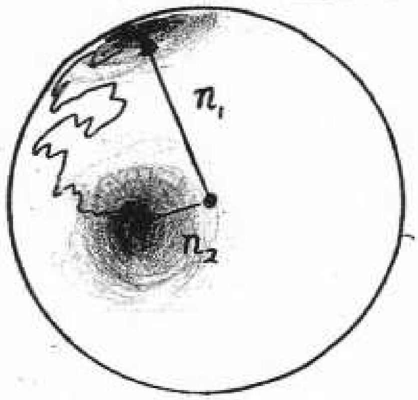
(i) <u>Formal Interpretation</u> : The path integral in (110) can be written in the usual way as a product over infinitesimal time integrals:

$$K(n_2, n_1 ; t_2 t_1) = \lim_{N\to\infty} \left(\frac{2S+1}{4\pi} \right)^{N-1} \prod_{j=1}^{N-1} \int d\underline{\Omega}_j \, e^{\frac{i}{\hbar} S[\underline{\Omega}(t_j)]} \qquad (116)$$

where $S[\underline{n}(t)]$ is the action :
$$S = \int dt\, L(\Omega, \dot{\Omega}; t) \qquad (117)$$

and $\Omega_j \equiv \Omega(t_j)$, with
$$\left.\begin{aligned} t_j &= t_{in} + j\epsilon_N \\ \epsilon_N &= \frac{t_f - t_{in}}{N} \end{aligned}\right\} \qquad (118)$$

This expression is to be interpreted in the same way as a traditional path integral, with paths on the Bloch sphere. As with the standard path integral, the possible paths are arbitrary, but the way in which very "jagged" paths are suppressed is a little different. This is because the "kinetic" term in the Lagrangian is LINEAR in time derivatives, instead of quadratic. In Appendix to this section we study this point in a little more detail. We simply note here that the Hamiltonian in the path integral above should be interpreted as



A TYPICAL PATH ON
THE BLOCH SPIN SPHERE

$$\mathcal{H}[\underline{n}(t_j)] = \frac{\langle \underline{n}(t_j) | \mathcal{H}(t_j) | \underline{n}(t_{j-1}) \rangle}{\langle \underline{n}(t_j) | \underline{n}(t_{j-1}) \rangle} \qquad (119)$$

and the time evolution operator has matrix elements between states separated by ϵ in time given by

$$\left.\begin{aligned} \langle \underline{n}_j | \hat{\mathcal{U}}(t_j, t_{j-1}) | \underline{n}_{j-1} \rangle &\equiv \langle \underline{n}_j | \hat{T} e^{-i/\hbar \int_{t_{j-1}}^{t_j} dt\, H(t)} | \underline{n}_{j-1} \rangle \\ &= \langle \underline{n}_j | \underline{n}_{j-1} \rangle\, e^{-i/\hbar\, \epsilon \mathcal{H}[\underline{n}(t_j)]} \end{aligned}\right\} \qquad (120)$$

The key question then is the overlap between adjacent state vectors in the path integral - it is a straightforward exercise to show that

$$\left.\begin{aligned} \langle \underline{n}_j | \underline{n}_{j-1} \rangle &= e^{iS(\dot{\phi} \cos\theta)\epsilon} \\ &\equiv e^{i\underline{A} \cdot \left(\frac{d\underline{n}}{dt}\right)\epsilon} \end{aligned}\right\} \qquad (121)$$

and so the overlap integral falls off linearly with the "spin velocity" $d\underline{n}/dt$.

We note that by using (120) & (121) we immediately have a derivation of (116), starting from the more usual expression for $K(\underline{n}_2, \underline{n}_1; t_2, t_1)$ written in terms of the time evolution operator, ie, starting from

$$\left.\begin{aligned} K(\underline{n}_2, \underline{n}_1; t_2 t_1) &= \langle \underline{n}_2 | \hat{\mathcal{U}}(t_2, t_1) | \underline{n}_1 \rangle \\ &= \lim_{N \to \infty} \left(\frac{2S+1}{4\pi}\right)^N \prod_{j=1}^{N-1} \int d\underline{\Omega}_j \langle \underline{\Omega}_j | \hat{T} e^{-i/\hbar \int_{t_{j-1}}^{t_j} dt\, H(t)} | \underline{\Omega}_{j-1} \rangle \end{aligned}\right\} \qquad (122)$$

(ii) Physical Interpretation : Suppose we now return to the action in (117), and evaluate it by doing the time integral. We then have the result.

$$\left.\begin{aligned} S &= \int_{t_1}^{t_2} dt \left[S\underline{A}\cdot\frac{d\underline{n}}{dt} - \mathcal{H}(S\underline{n}(t))\right] \\ &= S\tilde{\omega}_{21} - \int dt\, \mathcal{H}(S\underline{n}(t)) \end{aligned}\right\} \qquad (123)$$

where the geometric phase $\tilde{\omega}_{21}$ is

$$\tilde{\omega}_{21} = \int_{n_1}^{n_2} \underline{A}\cdot d\underline{n} \qquad (124)$$

Notice that because $A \sim O(\hbar)$, this phase disappears in the classical limit. We also notice that we can derive the equation of motion for the spin from this form, or from the Lagrangian we gave in eqtns (113) - (115). It is straightforward to show, starting from these eqtns., that we get the eqtn of motion

$$\dot{\underline{n}}(t) = -\dot{\underline{n}} \times \frac{\partial \mathcal{H}}{\partial \underline{n}} \qquad (125)$$

or, if we define the CLASSICAL vector $\underline{S} = S\underline{n}(t)$, we have

$$\dot{S}(t) = -\underline{S} \times \frac{\partial \mathcal{H}}{\partial \underline{S}} \qquad (126)$$

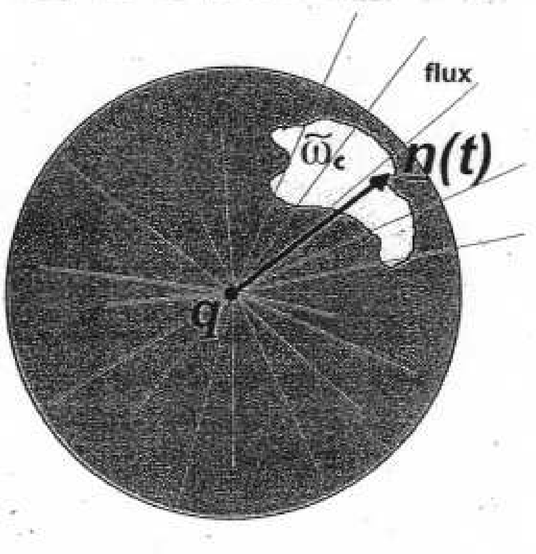
The physical interpretation of the geometric phase in (124) is particularly clear if we assume a closed path for the trajectory (as we would in calculating, eg., the thermodynamics of the system. In this case we have

$$\left.\begin{aligned} \tilde{\omega}_c &= \oint_C d\underline{n}\cdot\underline{A} \\ &= \hbar\Omega_c \end{aligned}\right\} \qquad (127)$$

so that the total geometric phase which is accumulated around the contour C is just $\hbar S\Omega_c$, where Ω_c is the SOLID ANGLE (modulo 4π) swept out by the curve. The fact that the angle is only defined modulo 4π means that

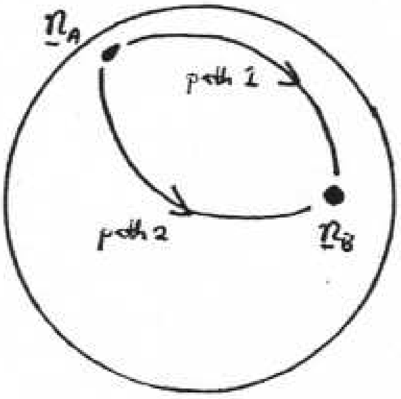
$$e^{4i\pi S} = 1 \quad\Rightarrow\quad S = \left.\begin{matrix} n \\ n+\frac{1}{2}\end{matrix}\right\} \qquad (128)$$

ie., that S must be integer or half-integer in value.



MOTION OF $\underline{n}(t)$ AROUND A CONTOUR C, IN FIELD OF A MONOPOLE w/ CHARGE $q = \hbar S$

Notice another interesting consequence of this. Suppose the system can preferentially follow one of several paths between 2 points on the Bloch sphere. Then, as shown in the diagram, we can imagine considering only these dominant paths in the path integral. The transition amplitude from $\underline{n}_A$ to $\underline{n}_B$, if only 2 paths are important, is then just



SITUATION WHERE THE SPIN PATH INTEGRAL FOR TRANSITIONS FROM $|\underline{n}_A\rangle$ to $|\underline{n}_B\rangle$ IS DOMINATED BY 2 PATHS (& FLUCTUATIONS AROUND THESE).

$$\left.\begin{aligned} \langle \underline{n}_B | \hat{U} | \underline{n}_A \rangle &\sim t^{(1)}_{BA} + t^{(2)}_{BA} \\ &\sim \left[A_1 e^{i/\hbar S^{(1)}_{BA}} + A_2 e^{i/\hbar S^{(2)}_{BA}} \right] \end{aligned}\right\} \quad (129)$$

The most interesting case arises when $|A_1| \sim |A_2|$, in which case we have

$$\langle n_B | \hat{U} | n_A \rangle \sim A \cos \delta\tilde{\Omega}_c S \qquad (130)$$

where $\delta\tilde{\Omega}_c$ is the solid angle area enclosed between the 2 paths. This is just an "Aharonov-Bohm" effect in spin space.

This concludes our simple discussion of spin path integrals - now we will employ them on a few examples, to see how they can be useful.

(b) Tunneling & Path Integral Theory :

It is very interesting to make the connection to the previous perturbative work on spin dynamics. As a bonus we learn how to do tunneling problems with path integrals, using a slight adaptation which has come to be known as the "instanton method". Thus we will first look at tunneling using path integrals, and then at a tunneling spin in the next subsection.

(i) Instanton Method : This is a method which is really equivalent to WKB theory, but is much more intuitively clear. It can be used in both particle mechanics and field theory, but here it will be introduced briefly only for particle mechanics.

The instanton method begins by changing all paths in a path integral to imaginary time, i.e., $t \to i\tau$, so that we now look at

$$\left.\begin{aligned} \langle q_f | U(i\tau) | q_i \rangle &\equiv \langle q_f | e^{-H\tau/\hbar} | q_i \rangle \\ &\equiv \sum_m \langle q_f | m \rangle e^{-\epsilon_m \tau/\hbar} \langle m | q_i \rangle \\ &\equiv \int_{q_i}^{q_f} \mathcal{D}q(\tau)\, e^{-\bar{S}/\hbar} \end{aligned}\right\} \quad (131)$$

where the $\{|m\rangle\}$ are the eigenstates of the system. This manoeuvre was originally introduced by Feynman so as to use path integrals for statistical mechanics calculations, but here we use it to calculate the energies of the lowest-lying states of the system, and to find tunneling amplitudes. Note the new form of the action in (131); we have

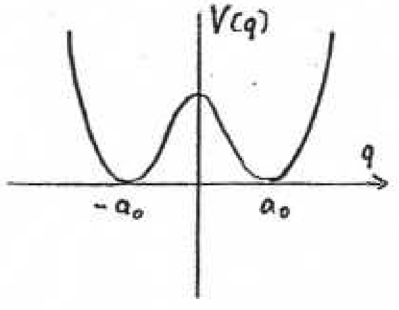
$$\bar{S}_c = \int d\tau \, L\left(q, -i\frac{dq}{d\tau}\right) \tag{132}$$

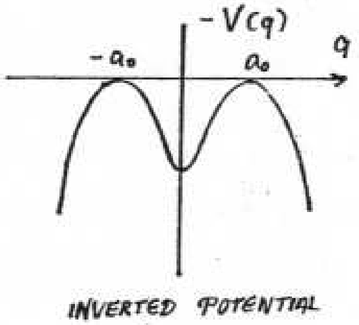
which for ordinary particle mechanics gives

$$\bar{S}_c = \int d\tau \left[\tfrac{1}{2} m \dot{q}^2 + V(q)\right] \tag{133}$$

This is tantamount to saying that we are now looking at particle dynamics in an inverted potential, ie., $V(q) \to -V(q)$.

The easiest thing to do is look at a simple example, that of the standard 2-well potential shown below. This is a standard problem in semiclassical WKB theory. The form of the potential is not too important - if we want to do explicit calculations it is convenient to use a "q^4" form, viz.:





INVERTED POTENTIAL

$$V(q) = V_0\left[-\tfrac{1}{2}\left(\frac{q}{a_0}\right)^2 + \tfrac{1}{4}\left(\frac{q}{a_0}\right)^4\right] \tag{134}$$

which has minima at $q = \pm a_0$, and a maximum at $q = 0$. In the standard WKB treatment, one finds that the "ground-state splitting", between the symmetric & anti-symmetric combinations of states that are localised in each well, is given by

$$\left.\begin{aligned} \hbar\Delta_0 &\sim \hbar \frac{\omega_0}{\pi} \exp\left[-\frac{1}{\hbar}\int_{-a_0}^{a_0} dq \, |p(q)|\right] \\ \text{where} \quad |p(q)|^2 &= 2m\left(V(q) - E_0\right) \; ; \quad ; \; E_0 = \frac{\hbar\omega_0}{2} \end{aligned}\right\} \tag{135}$$

and ω_0 is the frequency of small oscillations in each potential well. The energies of the 2 states are thus

$$E_{\pm} = E_0 \pm \hbar\Delta_0/2 \tag{136}$$

Now consider how we look at this problem in path-integral / instanton language. Let's first recall briefly how we do a simple path integral calculation in ordinary time. We will be specifically interested in the semi-classical regime, ie., in the limit of small $\hbar$, where we are interested in the lowest-order (in $\hbar$) deviations from classical behaviour. In a path integral calculation this corresponds to small deviations from the classical path(s), in which the change in action from the classical value $\bar{S}_c$ is $\sim O(\hbar)$ or less. Suppose we define the path by

$$q(t) = q_c(t) + x(t) \quad = \quad q_c(t) + \sum_n a_n x_n(t) \tag{137}$$

where the $\{x_n(t)\}$ are a set of orthonormal basis functions satisfying

$$\left.\begin{aligned} \int_{t_i}^{t_f} dx\, x_n(t)\, x_{n'}(t) &= \delta_{nn'} \\ x_n(t_f) = x_n(t_i) &= 0. \end{aligned}\right\} \quad (138)$$

The classical path $q_c(t)$ is defined by the usual condition $\delta S/\delta q_c = 0$, ie., by Lagrange's eqtns. for $q_c(t)$. However in the path integral we need to know the weight assigned to the deviation $x(t)$ from $q_c(t)$, which for small deviations is found by computing

$$\left.\begin{aligned} S[q(t)] &= S[q_c(t)] + \int dt \frac{\delta S}{\delta q}\Big|_{q=q_c} x(t) + \frac{1}{2}\int dt \frac{\delta^2 S}{\delta q^2}\Big|_{q=q_c} x^2(t) + \cdots \\ &= S_c + \frac{1}{2}\int dt \frac{\delta^2 S}{\delta q^2}\Big|_{q=q_c} x^2(t) + \cdots \end{aligned}\right\} \quad (139)$$

where the linear vanishes by hypothesis, and we stop here at 2nd order. Now consider the path integral we defined in (108), and expand it about the classical path. We have

$$\left.\begin{aligned} K(q_2, q_1; t_f, t_i) &= A(t_f, t_i)\, e^{i/\hbar\, S_c} \\ A(t_f, t_i) &= \int_{x(t_i)=0}^{x(t_f)=0} \mathcal{D}x(t)\, e^{\frac{i}{\hbar}\int_{t_i}^{t_f} dt \left[\frac{1}{2}\frac{\delta^2 S}{\delta q^2}\big|_{q=q_c} x^2(t)\right]} \end{aligned}\right\} \quad (140)$$

As an example let's suppose that $\qquad L = \frac{1}{2}m\dot{q}^2 - V(q) \qquad (141)$

In this case it is fairly easy to get the following results for $A(t_f, t_i)$:

$$A(t_f, t_i) = \int_{x(t_i)=0}^{x(t_f)=0} \mathcal{D}x(t)\, e^{i/\hbar \int_{t_i}^{t_f} dt \left[\frac{1}{2}m\dot{x}^2 - \frac{1}{2}\frac{d^2V}{dq^2}\big|_{q=q_c} x^2\right]} \qquad (142)$$

which shows that the orthonormal functions $x_n(t)$ in (138) are just harmonic oscillator eigenfunctions satisfying

$$\left[m\frac{d^2}{dt^2} + \frac{d^2V}{dq^2}\Big|_{q=q_c}\right] x_n(t) = \omega_n x_n(t) \qquad (143)$$

which is what we expect since we are simply doing a saddle-point integration. It then follows by doing the Gaussian integration that

$$A(t_f, t_i) = \frac{1}{\sqrt{\det\left(m\frac{d^2}{dt^2} + V''(q_c)\right)}} \equiv \prod_{n=1}^{\infty} \frac{1}{\omega_n^{1/2}} \qquad (144)$$

This is a standard result from path integral theory – the $x_n(t)$ are just the vibrational "string" modes of the path deviations around the classical path. We have recalled these details of path integral theory in ordinary time so as to quickly see how it then works in imaginary time. If we now go back to eqtns. (132) & (133), we see that we can go through exactly the same development, but now assuming that $V(q) \to -V(q)$; and we get

$$\breve{K}(q_2, q_1; \tau_f, \tau_i) = \bar{A}(\tau_f, \tau_i)\, e^{-\tilde{S}_c/\hbar} \tag{145}$$

where $\tilde{S}_c$ is the tunneling action given in (132), (133), and

$$\bar{A}(\tau_f, \tau_i) = \int_{\bar{x}(\tau_i)=0}^{\bar{x}(\tau_f)=0} \mathcal{D}\bar{x}(\tau)\; e^{-\frac{1}{\hbar}\int_{\tau_i}^{\tau_f} d\tau \left[\frac{1}{2}\frac{\delta^2 \tilde{S}}{\delta q^2}\Big|_{q=\bar{q}_c} \bar{x}^2(\tau)\right]} \tag{146}$$

$$\left.\begin{aligned} &\xrightarrow[L=\frac{1}{2}m\dot{q}^2 - V(q)]{} \int_{\bar{x}_i=0}^{\bar{x}_f=0} \mathcal{D}x(\tau)\; e^{-1/\hbar \int d\tau \left[\frac{1}{2}m\dot{\bar{x}}^2 + \frac{1}{2}\frac{d^2V}{dq^2}\Big|_{q=\bar{q}_c}\bar{x}^2\right]} \\ &= \frac{1}{\sqrt{\det\left(-m\frac{d^2}{d\tau^2} + V''(q_c)\right)}} \equiv \prod_{n=1}^{\infty} \frac{1}{\tilde{\omega}_n^{1/2}} \end{aligned}\right\} \tag{147}$$

where $\bar{x}(\tau)$ describes the deviations from the "classical" tunneling path $\bar{q}_c(\tau)$, and the $\tilde{\omega}_n$ are the eigenvalues of the SHO differential eqtn in the inverted potential:

$$\left[-m\frac{d^2}{d\tau^2} + \frac{d^2V}{dq^2}\Big|_{q=\bar{q}_c}\right]\hat{x}_n(t) = \tilde{\omega}_n \hat{x}_n(t) \tag{148}$$

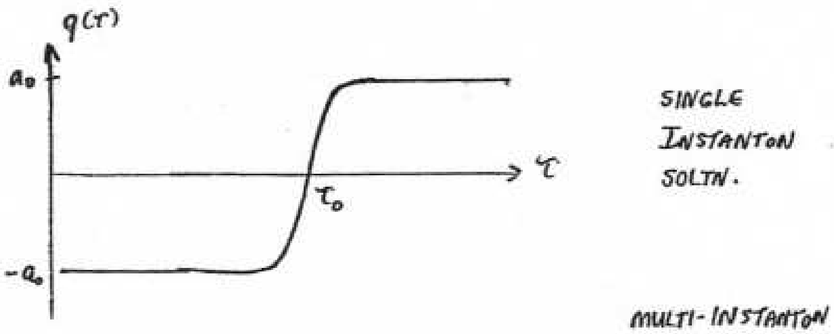
(ii) 2-Well System: Effective Hamiltonian & Tunneling Dynamics: We return to the 2-well model in (134), and apply the path integral method to it. First we need the classical solutions in the inverted potential. These are easy, since the problem is very similar to the Sine-Gordon model. The simplest classical solution starts at $q = -a_0$ for $\tau_i \to -\infty$, and then rolls over to $q = a_0$ for $\tau_f \to \infty$. This solution is localized around some time τ_0, and the solution itself is found from solving the eqtn of motion in the inverted potential - one gets:

$$\bar{q}_c(\tau) = a_0 \tanh\left[\tfrac{1}{2}\Omega_0(\tau - \tau_0)\right] \tag{149}$$

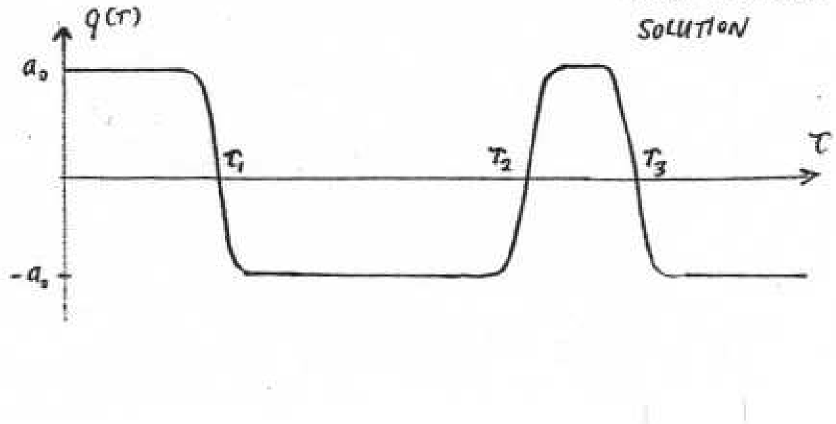
where the "bounce frequency", or inverse "bounce time" is

$$\Omega_0 = 1/\tau_B = \frac{1}{a_0}\sqrt{\frac{2V_0}{m}} \tag{150}$$

The "anti-instanton" solution goes the other way, from $q(\tau_i = -\infty) = a_0$ to $q(\tau_f = \infty) = -a_0$. We also see



SINGLE INSTANTON SOLTN.



MULTI-INSTANTON SOLUTION

that there are "multi-instanton" solutions where the particle bounces back & forth between the 2 peaks at ± a_0. Finally there are unstable solutions which we ignore here.

The exact form of the instanton solution is not terribly important here - what matters is that there is a finite classical action associated with it, given by

$$\tilde{S}_o = \int_{-a_0}^{a_0} dq \left[2m V(q) \right]^{1/2} \qquad (151)$$

With these preparatory remarks concerning the 2-well system, we can now determine the low-energy effective Hamiltonian, & the resulting tunneling dynamics.

* Effective Hamiltonian: There are many ways, starting from some high-energy effective Hamiltonian, to derive another low-energy effective Hamiltonian. Among those we have seen in previous sections we recall (a) simple perturbation theory; (b) canonical transformation; and (c) continuation arguments like those used for Fermi liquid theory, which are based on a combination of perturbation theory and semi-classical expansions. There are quite a few other ways in which one can formally truncate a Hamiltonian to low energies. These include renormalisation group & other scaling methods involving scaling, which involve incremental removal of high-energy and/or short wavelength excitations, and Born-Oppenheimer methods, which distinguish fast & slow variables, integrating out the former.

Here we employ a semiclassical instanton method to find the low-energy effective Hamiltonian. We will do this in 2 ways, one for the simple 1-dimensional 2-well problem here, and the other for the tunneling spin.

To address the 1-d 2-well problem, we consider the expression for the imaginary time transition amplitude in (131), and look at the long-time limit. We are interested in transitions between states localised in one or other of the 2 wells - we use the notation

$$|a_0\rangle \equiv |\Uparrow\rangle \qquad |-a_0\rangle \equiv |\Downarrow\rangle \qquad (152)$$

and we want

$$T_{\downarrow\uparrow} = \langle \Downarrow | e^{-\mathcal{H}T/\hbar} | \Uparrow \rangle \qquad (153)$$

in the limit where $T \rightarrow \infty$ (in practise, we want $T^{-1} \lesssim \Delta_o$, where Δ_o is the low frequency scale associated with the tunneling). We note from the 2nd form in (131) that in this limit we expect

$$T_{\Downarrow\Uparrow}(T) = \langle \Downarrow | e^{-\mathcal{H}T/\hbar} | \Uparrow \rangle \xrightarrow[\Delta_o T \gtrsim 1]{} C e^{-E_o T/\hbar} \left(e^{\Delta_o T} - e^{-\Delta_o T} \right) \qquad (154)$$

where C is a constant; and we expect:

$$T_{\Uparrow\Uparrow}(T) = \langle \Uparrow | e^{-\mathcal{H}T/2} | \Uparrow \rangle \xrightarrow[\Delta_o T \gtrsim 1]{} C e^{-E_o T/\hbar} \left(e^{\Delta_o T} + e^{-\Delta_o T} \right) \qquad (155)$$

We get these results by assuming that all higher states are separated by energies >> $\hbar\Delta_o$ from the 2 lowest levels, and by assuming that the 2 lowest states are given to good accuracy by

$$|\pm\rangle \sim \frac{1}{\sqrt{2}} \left(|\Uparrow\rangle \mp |\Downarrow\rangle \right) \qquad (156)$$

where $|\pm\rangle$ are the eigenstates with energies $E_\pm$ in (136). If we stay in the subspace of these 2 lowest levels, then our effective Hamiltonian is extremely simple – we have

$$\hat{\mathcal{H}}^0_{eff} = |\sigma\rangle \mathcal{H}^{\sigma\sigma}_{eff} \langle\sigma'| \quad ; \qquad \mathcal{H}^{\sigma\sigma'}_{eff} = \hbar \begin{pmatrix} 0 & \Delta_0 \\ \Delta_0 & 0 \end{pmatrix} \tag{157}$$

where $|\sigma\rangle = |\Uparrow\rangle, |\Downarrow\rangle$, and we subtract off the constant energy shift E_0.

Our task is to evaluate Δ_0. To do this we calculate directly the amplitude $T_{\downarrow\uparrow}$ from the original Hamiltonian (134), using the instanton method – this means calculating the sum over all possible paths back & forth between $|\Uparrow\rangle$ and $|\Downarrow\rangle$ (starting with up and finishing with $|\Downarrow\rangle$), and then including the small fluctuations around these. The paths are of the type shown in the Figure on p. 41, and the fluctuations will lead to a "fluctuation determinant" like (147).

There are well-known tutorial discussions of this evaluation in the literature (notably by Coleman & Schulman), so here I will just summarize the main lines of the derivation:

– First, the "classical action" for a path containing m tunneling events (note that in calculating $T_{\downarrow\uparrow}$ we require $m = 2n+1$, where $n = 0,1,2,\ldots$). This is easy – the action contributed by the stationary states $|\Uparrow\rangle$ and $|\Downarrow\rangle$ is zero (since their classical energy is zero), and each instanton contributes $\tilde{S}_0$, from (151). So we get a total contribution, for a path with n flips, given by

$$\tilde{S}_{cl}(m) = m\tilde{S}_0 \qquad (m = 2n+1). \tag{158}$$

– The fluctuations we must consider are of 2 kinds. First, there is the fluctuation in the positions of the n instantons. Then, there are the small path oscillations around these positions. These contributions must be multiplied together. Thus our final answer will be

$$T_{\downarrow\uparrow} = A_0^{std.} \sum_{n=0}^{\infty} A^{kink}_{\downarrow\uparrow}(2n+1)\, e^{-(2n+1)\tilde{S}_0/\hbar} \tag{159}$$

where A_0^{std} refers to fluctuations around the stationary states $|\Uparrow\rangle$ and $|\Downarrow\rangle$, $A^{kink}_{\downarrow\uparrow}(2n+1)$ refers to the fluctuations of the kinks (i.e., instantons) themselves, and this is all multiplied by the classical action. The kink contribution involves 2 contributions – fluctuations of the kink positions, over which we must integrate, and small oscillations about the classical kink profile itself. Thus we can write

$$\left.\begin{aligned} A^{kink}_{\downarrow\uparrow}(2n+1) &= \prod_{\ell=1}^{2n+1} \int_{-T/2}^{\tau_{\ell+1}} d\tau_\ell \; \mathcal{D}_0^{\ell} \\ &\equiv \int_{-T/2}^{T/2} d\tau_{2n+1} \int_{-T/2}^{\tau_{2n+1}} d\tau_{2n} \cdots \int_{-T/2}^{\tau_2} d\tau_1 \; \mathcal{D}_0^{\ell} = \frac{(\mathcal{D}_0 T)^{2n+1}}{(2n+1)!} \end{aligned}\right\} \tag{160}$$

where the determinant $\mathcal{D}_0$ evaluates the fluctuations about a single kink profile. Summing the series, we have

$$T_{\downarrow\uparrow} = A_0^{std} \tfrac{1}{2}\left(e^{\mathcal{D}_0 T e^{-S_0/\hbar}} - e^{-\mathcal{D}_0 T e^{-S_0/\hbar}} \right) \tag{161}$$

from which we see that Δ_0 in (136) and (154) is given by

$$\Delta_0 = \mathcal{D}_0 e^{-\bar{S}_0/\hbar} \tag{162}$$

and that we can extract E_0 from an evaluation of A_0^{stat}. The evaluation of these determinants is left as an exercise - one finds for $\mathcal{D}_0$ that:

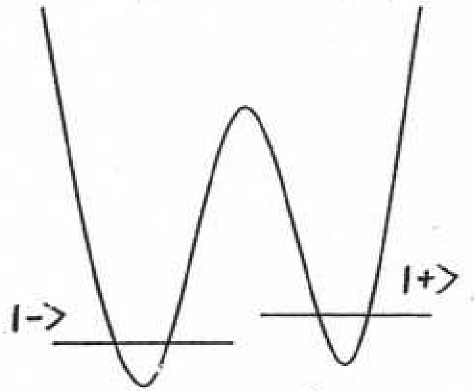
$$\mathcal{D}_0 = \left(\frac{\bar{S}_0}{2\pi\hbar}\right)^{1/2} \left| \frac{\det\left(-d^2/dt^2 + \omega_0^2\right)}{\det'\left(-d^2/dt^2 + V''(q_c)\right)} \right|^{1/2} \tag{163}$$

where ω_0 is, as before, the small oscillation frequency in each well, and the notation det′ indicates that the "zero mode" (ie., the oscillation of the centre of mass position of the instanton) is to be omitted from the determinant (it is already in the summation over instanton positions in (160)). For A_0^{std} we get

$$A_0^{std} = \left(\frac{\omega_0}{\pi\hbar}\right)^{1/2} e^{-\frac{\omega_0}{2}T} \tag{164}$$

so that $E_0 = \hbar\omega_0/2$, as we already found in (135).

Note finally that if we add an external bias to the 2 well system, so that $V(q)$ in (134) is replaced by



SEE EQTN (179) FOR DEFN OF $|\pm\rangle$

$$V(q) = V_0\left[-\tfrac{1}{2}(q/a_0)^2 + \tfrac{1}{4}(q/a_0)^4\right] + H_0 q \tag{165}$$

then we get a new effective Hamiltonian

$$\left.\begin{aligned} \hat{\mathcal{H}}_{eff} &= |\sigma\rangle \mathcal{H}_{eff}^{\sigma\sigma'} \langle\sigma'| \\ \mathcal{H}_{eff}^{\sigma\sigma'} &=: \hbar\begin{pmatrix} \epsilon_0 & \Delta_0 \\ \Delta_0 & -\epsilon_0 \end{pmatrix} \end{aligned}\right\} \tag{166}$$

with

$$\epsilon_0 = a_0 H_0/\hbar \ll \omega_0 . \tag{167}$$

where the restriction $\epsilon_0 \ll \omega_0$ stops any mixing of the 2 lowest levels with any of the higher levels in the original problem.

* <u>Tunneling Dynamics of 2-state system</u>: From the effective Hamiltonian for the 2-state system we can now trivially calculate its dynamics using standard elementary quantum mechanics. Thus we want to calculate

$$\left.\begin{aligned} K^0_{\sigma\sigma'}(t) &= \hat{T}\langle\sigma| e^{-i\hat{\mathcal{H}}_{eff}t/\hbar} |\sigma'\rangle \\ &\equiv \langle\sigma| \hat{T} \exp\{-it[\epsilon_0\hat{\tau}_z + \Delta_0\hat{\tau}_x]\} |\sigma'\rangle \end{aligned}\right\} \tag{168}$$

This is fairly straightforward to evaluate by expanding the exponentials in a power series. However it is interesting to derive the results in a slightly different way, as follows.

First, consider the time evolution operator for infinitesimal time - then we have

$$\hat{U}(dt) = \exp\{-i(\epsilon_0\hat{\tau}_z + \Delta_0\hat{\tau}_x)\,dt\} = 1 - i(\epsilon_0\hat{\tau}_z + \Delta_0\hat{\tau}_x)\,dt \qquad (169)$$

from which we see that we get a contribution $-i\Delta_0\,dt$ if the system flips, and a contribution $\mp i\epsilon_0\,dt$ if the system is in one of the stationary states $|\Uparrow\rangle$ or $|\Downarrow\rangle$ respectively. It is then simple to evaluate the result - we get

- <u>Symmetric Case</u> $(\epsilon_0 = 0)$

$$K_0^{\sigma\sigma}(t) = \sum_{n=0}^{\infty}\int_0^t dt_{2n}\int_0^{t_{2n}} dt_{2n-1}\cdots\int_0^{t_2} dt_1\,(-i\Delta_0)^{2n} = \cos\Delta_0 t \qquad (170$$

$$K_0^{\sigma,-\sigma}(t) = \sum_{n=0}^{\infty}\int_0^t dt_{2n+1}\int_0^{t_{2n+1}} dt_{2n}\cdots\int_0^{t_2} dt_1\,(-i\Delta_0)^{2n+1} = -i\sin\Delta_0 t \qquad (171)$$

- <u>Biased Case</u> $(\epsilon_0, \Delta_0$ arbitrary$)$

$$\left.\begin{aligned} K_0^{\sigma\sigma}(t) &= \sum_{n=0}^{\infty}(-i\Delta_0)^{2n}\int_0^t dt_{2n}\,e^{-i\sigma\epsilon_0(t-t_{2n})}\int_0^{t_{2n}} dt_{2n-1}\,e^{-i\sigma\epsilon_0(t_{2n}-t_{2n-1})}\int\cdots \\ K_0^{\sigma,-\sigma}(t) &= \sum_{n=0}^{\infty}(-i\Delta_0)^{2n+1}\int dt_{2n+1}\,e^{-i\sigma\epsilon_0(t-t_{2n+1})}\int_0^{t_{2n+1}} dt_{2n}\,e^{+i\sigma\epsilon_0(t_{2n}-t_{2n-1})}\int\cdots \end{aligned}\right\} \qquad (172$$

and these sums can be evaluated by simple Laplace transformation of the convoluted integrals

$$K_0^{\sigma\sigma'}(t) = \int_{-i\infty}^{i\infty} dp\,e^{pt}K_0^{\sigma\sigma'}(p) \qquad (173)$$

Thus, eg., we get

$$\left.\begin{aligned} K_0^{\uparrow\uparrow}(p) &= \frac{1}{p - i\epsilon_0}\sum_{n=0}^{\infty}\frac{(-i\Delta_0)^{2n}}{(p^2+\epsilon_0^2)^n} \\ &= \frac{1}{p - i\epsilon_0}\,\frac{p^2+\epsilon_0^2}{p^2+E_0^2} \end{aligned}\right\} \qquad (174)$$

where

$$E_0^2 = \Delta_0^2 + \epsilon_0^2 \qquad (175)$$

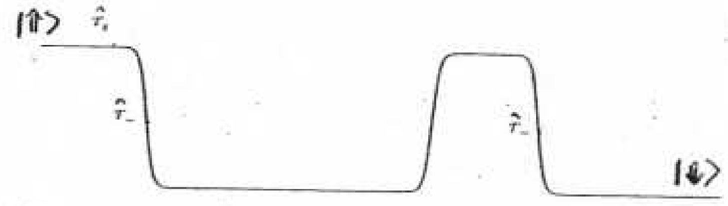
from which

$$K_0^{\uparrow\uparrow}(t) = \cos E_0 t - i\frac{\epsilon_0}{E_0}\sin E_0 t \qquad (176)$$

We notice 2 interesting things about these results. First, we have, for this very simple system, just done yet another path integral calculation! How can it now be so simple? The reason is that once we reduce the problem to the simple effective Hamiltonian in (166), there is no need to evaluate a fluctuation determinant. Thus, going back to our original form for the path integral in (108), we have

$$K_0^{\sigma\sigma'}(t) = \int_{x_i=\sigma'}^{x_f=\sigma}\mathcal{D}x(t)\,\exp\{i/\hbar\int dt\,L(x,\dot{x})\} \qquad (177)$$

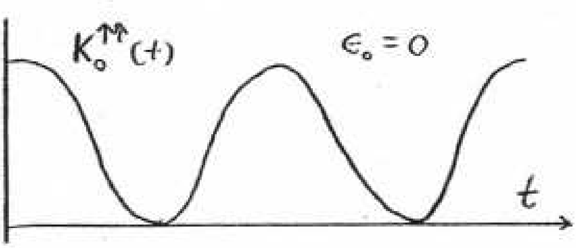
in which $x(t)$ is simply a set of paths in which the system "jumps" instantaneously between $|\Uparrow\rangle$ and $|\Downarrow\rangle$ at different times - there are no fluctuations about these paths because there are no other states for the system to fluctuate to, in this now very restricted Hilbert space. Nor is there any kinetic term in the Lagrangian - for this simple system we just have

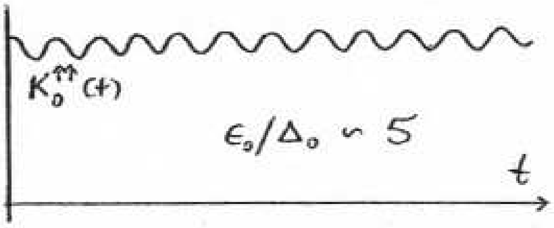


A TYPICAL INSTANTON PATH FOR THE 2-WELL SYSTEM. IN THE TRUNCATED 2-LEVEL SYSTEM, THE OPERATORS $\hat{\tau}_\pm$ CREATE INSTANTONS

$$L(x,\dot{x}) = -H(x,\dot{x}). \qquad (178)$$

where the "classical" $H(x,\dot{x})$ reduces to 2 possible values for $x(t)$; thus $x(t) \equiv \sigma(t)$, where $\sigma = \pm 1$.





The 2nd interesting thing about these results is the form of a correlation function like $K_0^{\Uparrow\Uparrow}(t)$ in (176). If we plot these, we see that when $\epsilon_0 = 0$, the system oscillates coherently between the 2 wells, with a period $t_0 = 2\pi/\Delta_0$, as one might expect. However adding the bias ϵ_0 tips the system out of resonance, and when $|\epsilon_0| \gg \Delta_0$, there is way for the system to make transitions from high to low energy, or indeed to tunnel at all, given the lack of resonance. There are small amplitude oscillations at a frequency $E_0/\hbar$, ie., at the frequency difference between the 2 eigenstates of the system, which in a finite bias have the form

$$|\pm\rangle = \frac{1}{[(E_\pm^0 + \epsilon_0)^2 + \Delta_0^2]^{1/2}} \left((E_\pm + \epsilon_0)\,|\Uparrow\rangle - \Delta_0\,|\Downarrow\rangle \right) \qquad (179)$$

where

$$E_\pm = \pm\sqrt{E_0^2} = \pm(\epsilon_0^2 + \Delta_0^2)^{1/2} \qquad (180)$$

Note that these eigenstates tend towards states localized in the left and right wells (ie., towards $|\Downarrow\rangle$ and $|\Uparrow\rangle$) when $|\epsilon_0| \gg \Delta_0$.

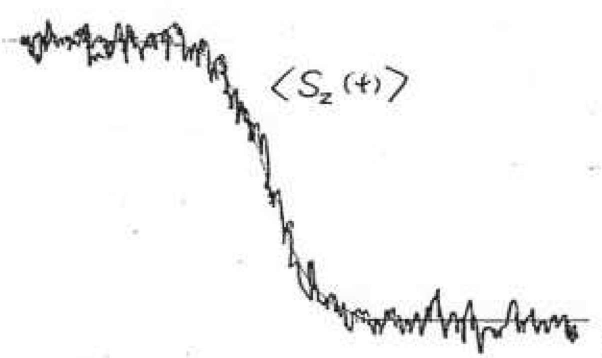
(c) Giant Spin: Tunneling Dynamics: Now we go back to the giant spin, and ask how to deal with its tunneling dynamics. As we saw above, there are 2 steps involved in doing this. The first is to derive the low-energy effective Hamiltonian (in particular an expression for Δ_0) and the second is to then find the dynamics. The second step is easy - we simply take over the results found above (eqtns (170) - (176)).

To derive the effective Hamiltonian we will take a particular example, the biaxial system we already examined in the context of the Fe-8 molecule. To make things pedagogically simple we will ignore the 4th order term, and use the Hamiltonian

$$\mathcal{H}_0(\underset{\sim}{S}) = -DS_z^2 + ES_x^2 \qquad (181)$$

for which already derived a perturbative result for the tunneling amplitude (cf. eqtn. (75)). One can also add an external field to this system, with very interesting results, which we will also look at.

(i) Zero-field Tunneling Problem : In this case we are dealing with tunneling between 2 coherent states $|\underline{n}_\uparrow\rangle$ and $|\underline{n}_\downarrow\rangle$, oriented along $\pm\hat{z}$ in spin space. Now, in the derivation of the low-energy effective Hamiltonian for such a problem in the last sub-section, we looked at the very long-time limit of the evolution in imaginary time. Here we will, as advertised on p.42, do it a little differently. Consider the time evolution operator $U(t)$, operating now in the low-energy subspace of 2 levels that we will be interested in, and now note that for intermediate times we will have



$$\left.\begin{aligned} U_{\sigma\sigma'}(t) &= \langle \underline{n}_\sigma | e^{-i\mathcal{H}_0(S\hat{\underline{n}})t} | \underline{n}_{\sigma'}\rangle \\ &\xrightarrow[\Delta_0^{-1} \gg t \gg \Omega_0^{-1}]{} \delta_{\alpha\beta} - it\langle\sigma|\mathcal{H}^0_{eff}|\sigma'\rangle \\ &\equiv \delta_{\alpha\beta} - it\,\mathcal{H}_{eff}^{\sigma\sigma'} \end{aligned}\right\} \text{(18}$$

THE ACTUAL TRACTORY FOLLOWED BY $S_z(t)$, BEFORE WE "COARSE-GRAIN" THE TIME

so that the tunneling matrix element is just

$$\Delta_0 = \frac{i}{t}U_{\sigma,-\sigma}(t) \qquad [\Delta_0^{-1} \gg t \gg \Omega_0^{-1}] \qquad (183)$$

The meaning of this result is seen in the figure - for intermediate times the very rapid oscillations which occur at time scales $\sim \Omega_0^{-1}$ are no longer relevant (here the UV frequency cut-off Ω_0 is of order the small oscillation frequency of the system around the 2 states $|\underline{n}_\uparrow\rangle$ or $|\underline{n}_\downarrow\rangle$).

We now want to find the amplitude

$$U_{\downarrow\uparrow}(t) = \int_{n(0)=|\uparrow\rangle}^{n(t)=|\downarrow\rangle} \mathcal{D}\underline{n}(t)\, e^{-1/\hbar \int_0^t d\tau\, \tilde{L}_0(n,\dot{n})} \qquad (184)$$

where we have rotated to imaginary time, and we use the Lagrangian in the form

$$\left.\begin{aligned} \tilde{L}_0(n,\dot{n}) &= -iS\dot{\theta}\phi\sin\theta - \tilde{\mathcal{H}}_0(S\underline{n}) \\ \tilde{\mathcal{H}}_0(S\underline{n}) &= S^2 D\left[\sin^2\theta + \frac{E}{D}\sin^2\theta\sin^2\phi\right] \end{aligned}\right\} (185)$$

where we are now using the Euclidean forms for L_0 and H_0, with the inverted potential as before.

The classical trajectories for this problem are easily found by looking at them from of the potential on the Bloch sphere - this was already shown before, and we show it again in the figure on the next page. We see that there are 2 paths, along the lines

$$\phi = 0, \pi \;; \qquad 0 \le \theta \le \pi \qquad (186)$$

between the north & south poles. Having fixed ϕ to be one or other of these values, we can eliminate it from L_0 in the integral, to find

$$\tilde{L}_0(\theta,\dot\theta) = \frac{\dot\theta^2}{4D} + S^2 E \sin^2\theta \qquad (\phi = 0, \pi). \qquad (187)$$

in which $2D$ now plays the role of a "mass". The instanton solution taking us from $|\Uparrow\rangle$ to $|\Downarrow\rangle$ is now easily found:

$$\left.\begin{aligned} \sin\theta(\tau) &= \operatorname{sech}(\omega_0\tau) \\ \omega_0 &= 2S\sqrt{(D+E)D} \end{aligned}\right\} \qquad (188)$$

where we see the small oscillation frequency emerge for the 1st time.

We do not go through the lengthy details here of the evaluation of the amplitude - one does it in much the same way as for the 2-well system, including the evaluation of the fluctuation determinant. The only new wrinkle is that we now have 2 paths, and as we saw above (cf. eqtns (129) and (130)), there is a relative phase between them. In fact the final answer is a sum over 2 paths $\eta = \pm$, with

$$\left.\begin{aligned} \Delta_0(S) &= \omega_0 \sum_{\eta=\pm} \left(\frac{2}{\pi}\mathrm{Re}\,\Phi_0^{(\eta)}\right)^{1/2} e^{-\Phi_0^{(\eta)}} \\ &\equiv \Delta_0 |\cos(\pi S)| \end{aligned}\right\} \qquad (189)$$

where the "phase" $\Phi_0^{(\eta)} \equiv \bar{S}_0^{(\eta)}/\hbar$ is given by

$$\Phi_0^{(\eta)} = 2S \ln\left[\left(\frac{D+E}{E}\right)^{1/2} + \left(\frac{D}{E}\right)^{1/2}\right] + i\pi\eta S \qquad (190)$$

so that the bare tunneling amplitude is, when $\mathbf{S}$ = integer:

$$\left.\begin{aligned} \Delta_0 &= \left(\frac{16}{\pi}\ln\left(\frac{4D}{E}\right)\right)^{1/2} D\, S^{3/2} \left(\frac{E}{4D}\right)^S \qquad [E \ll D] \\ \Delta_0 &= \left(\frac{32}{\pi}\right)^{1/2} D (DE)^{1/4} S^{3/2} e^{-2S(D/E)^{1/2}} \qquad [E \gg D] \end{aligned}\right\} \qquad (191)$$

The main features of note here are (i) the peculiar dependence of the exponent on S, and the way the exponent diverges as $\sim S(D/E)^{1/2}$ when $E \gg D$ (ii) the $S^{3/2}$ dependence of the prefactor; and of course most notably the fact that when $S = n + 1/2$ (1/2-integer spin), then from (189) we have no tunneling at all.

It is interesting to compare the results for $E/D \ll 1$ (ie, for weak tunneling and a very high barrier) with the perturbative results derived previously. They are close but not the same, and the study of why this is constitutes an interesting study in WKB vs. perturbation theory (compare (191) with (75)). It is also interesting to compare the result for Δ_0 in the small barrier limit with exact results - note that we can still apply WKB theory if $SD/E \gg 1$, since the barrier height is $\sim O(DS^2)$.

However the most striking feature of the results is of course the dependence on $|\cos \pi S|$. This remarkable result arises purely, in this formalism, from interference between the 2 tunneling paths - it is a Berry phase effect. We note that it has a much older interpretation, in terms of the famous theorem of Kramers concerning the existence of a ground state doublet (ie., 2 degenerate states as ground states) when $S = n + 1/2$. Kramers's theorem relies on time reversibility when there is no external applied field, which is what we have here.

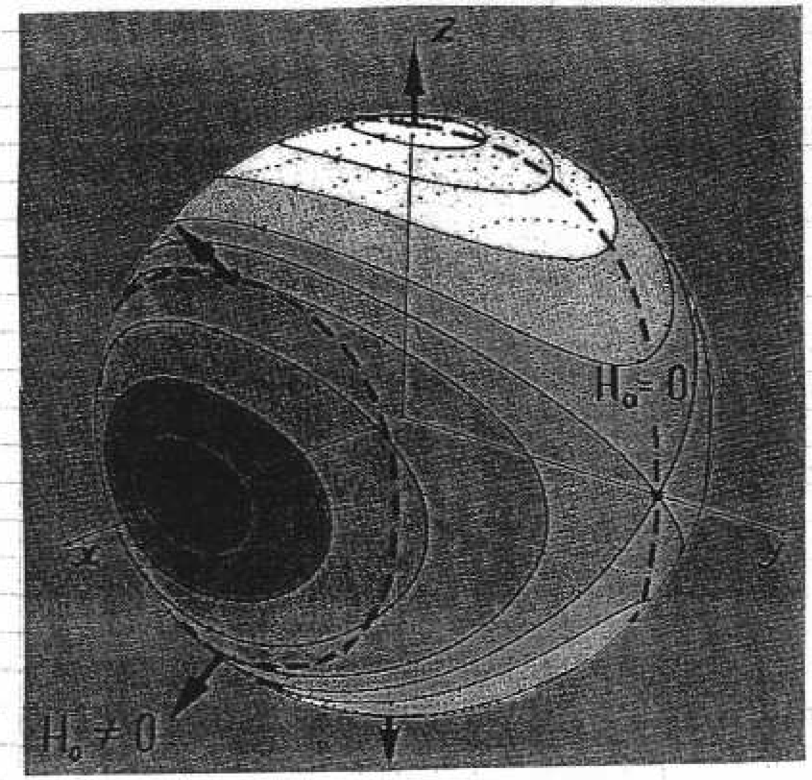
(ii) <u>Tunneling in a Finite Field</u>: Things start to get really interesting when we add an external field to the problem. One way to do this is by adding a longitudinal field H_0^z, which simply leads to a longitudinal bias

$$\epsilon_0 = g\mu_B S H_0^z \qquad (192)$$

which leads to an effective Hamiltonian in the form (166). Much more interesting results arise if we add a transverse field $\underline{H}_0^{\perp} = (H_0^x, H_0^y)$. The general analysis of this problem is complicated - here we study one special case, from which the general results become intuitively clear.

Consider the case where

$$\left.\begin{array}{c} |g\mu_B H| < D \\ E/D \gg 1 ; \quad SD/E \gg 1 \end{array}\right\} \qquad (193)$$



These restrictions tell us first that we still have tunneling, and second that we are in the strong tunneling regime, but still in the WKB limit.

The addition of the transverse fields adds an extra perturbation to the original Lagrangian $\mathcal{L}_0$ in (185). This is

$$\delta \tilde{\mathcal{L}}_M^{\perp} = -g\mu_B \underline{S} \cdot \underline{H}_0^{\perp} \qquad (194)$$

Let us begin with the case where $\underline{H}_0^{\perp} = x H_0$, so potential minima are at:

$$\phi_0 = 0 ; \quad \sin\Theta_0 = H_0^x / H_c \qquad (195)$$

$$g\mu_B H_c = 2(D+E)S \qquad (196)$$

This "symmetric" case is shown at left

In this symmetric case one can evaluate the tunneling amplitude analytically, but the details are rather complicated. The Lagrangian is now

$$\tilde{L}_0(n,\dot{n}) = iS\dot{\theta}\phi\sin\theta - \mathcal{H}_0(S\underline{n}) - \frac{H_0^x}{H_c}\sin\theta\cos\phi \tag{196}$$

and the final result for the tunneling amplitude is

$$\Delta_0(H_0^x) = \Delta_0(H_0^x)\,\left|\cos\left(\pi\Phi(H_0^x)\right)\right| \tag{197}$$

where the tunneling phase is

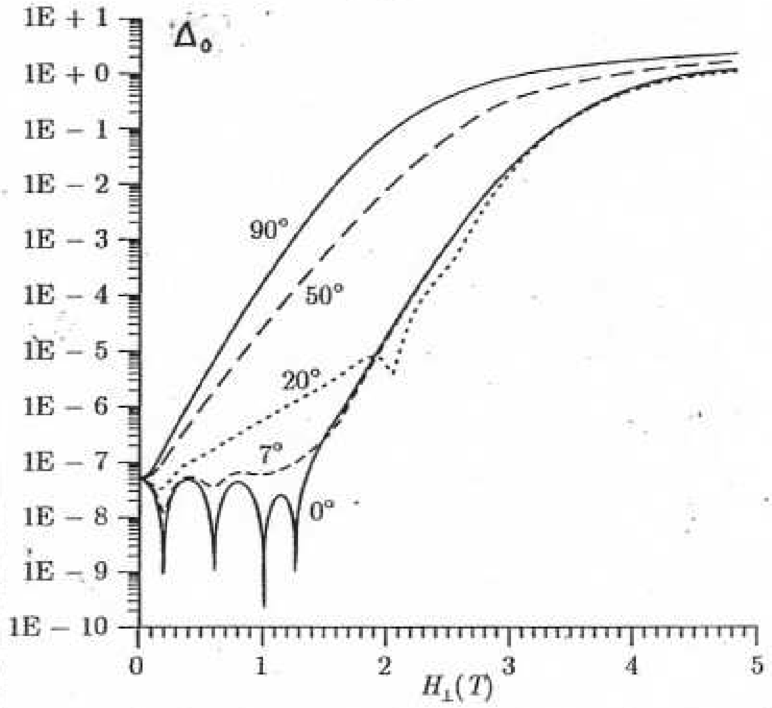
$$\left.\begin{aligned}\Phi(H_0^x) &= S\left[1-\left(\frac{D+E}{D}\right)^{\frac{1}{2}} H_0^x/H_c\right]\\ &\equiv S\left\{1-\frac{1}{\sqrt{D(D+E)}}\,\frac{\chi H_0^x}{2S}\right\}\end{aligned}\right\} \tag{198}$$

and $\Delta_0(H_0^x)$ increases very rapidly with H_0^x/H_c, as the tunneling paths become shorter and the barrier heights decrease.

Consider now what happens when we rotate the field away from the hard axis. Then the path which is nearest the hard axis has a large action - it is having to pass through a region of higher potential than the other path. We get a result (cf (129)):

$$\Delta_0(\underline{H}_0) = A_1 e^{i\Phi_1} + A_2 e^{i\Phi_2} \tag{199}$$

$$\text{where } (\Phi_1 - \Phi_2) = \Omega_c S \tag{200}$$



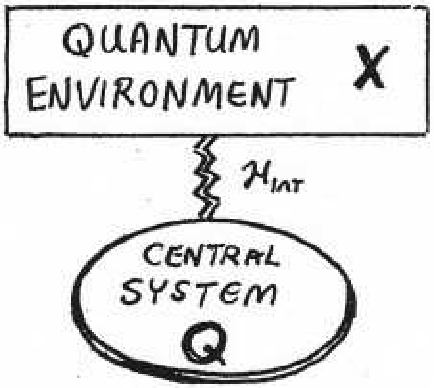
and Ω_c is the enclosed area on the Bloch sphere between the paths - but typically $A_1 \gg A_2$, where path I is the easiest path.

Thus we expect the oscillations to rapidly disappear, as we rotate away from the hard axis. An example is shown at left.

This phenomenon of "topological quenching" of the tunneling, by applying a field, is basically an "Aharonov-Bohm effect" in SPIN SPACE. It is seen in experiments on quantum relaxation, to be discussed later on. It is perhaps the most dramatic example of Berry phase effects for spin.

A.2.2. DYNAMICS OF THE SPIN-BOSON MODEL

Both the spin-boson model, to be discussed here, and the central spin model, to be discussed in the next section, are examples of problems where one wishes to integrate out or average over, in some way, the behaviour of an "environment", and then calculate the reduced density matrix of the system we are interested in. Thus we are interested in understanding the dynamics of mathematical models like the scheme at left, and the tool of choice is the quantity



$$\rho_s(Q,Q';t) = Tr_E\{\boldsymbol{\rho}(Q,Q';X,X';t)\} \qquad (201)$$

where the variables Q, Q' refer to the system, and the variables X, X' refer to the environment. The way the trace is carried out depends on what we know or are allowed to control in the state of the environment.

There are many ways of actually evaluating the dynamics of $\hat{\rho}$. If we are interested in non-perturbative work then the most useful is the path integral method, which works as follows:

- Free System : When we can ignore the environment, we just have the following simple propagator for the free system:

$$\rho_0(Q,Q';t) = \int dQ_0 \int dQ_0' \; K_0(Q,Q';Q_0,Q_0';t,t_0)\, \rho_0(Q_0,Q_0';t_0) \qquad (202)$$

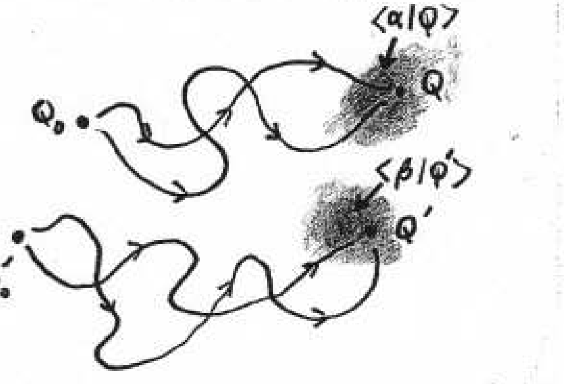
with

$$K_0(Q,Q';Q_0,Q_0';t,t_0) = \int_{q(t_0)=Q_0}^{q(t)=Q} \mathcal{D}q(\tau) \int_{q'(t_0)=Q_0}^{q'(t)=Q'} \mathcal{D}q'(\tau)\; e^{i/\hbar (S_0[q]-S_0[q'])} \qquad (203)$$

where

$$S_0[q] = \int d\tau\, L_0(q,\dot{q};\tau) \qquad (204)$$

is the action for the free system. These formulae are easy to understand;



PROPAGATION of $\hat{\rho}$ FROM $\rho(Q_0,Q_0')$ TO $\rho(Q,Q')$, ALONG DIFFERENT PATHS IN q-SPACE. THE OVERLAPS $\langle\alpha|Q\rangle$ AND $\langle\beta|Q'\rangle$ ARE ALSO SHOWN

$$\rho_0(Q,Q';t) = \langle Q|\psi(t)\rangle\langle\psi(t)|Q'\rangle \qquad \text{(205}$$

which is just a simple product, over the time evolution of $\psi(Q)$ and $\psi^*(Q')$. As before, if we want to calculate the matrix elements and dynamics of $\hat{\rho}_0$ between other states, we simply write

$$\rho_{\alpha\beta}(t) = \int dQ \int dQ' \langle\alpha|Q\rangle\, \rho_{QQ'}(t) \langle Q'|\beta\rangle \qquad \text{(20}$$

These results have the simple diagrammatic interpretation shown at left.

- <u>System plus Environment</u> :- Now we have a more complicated form for the entire "system + environment", with

$$L_{Total} = L_0[q\dot{q}) + L_{int}(q,\dot{q};X,\dot{X}) + L_E(X,\dot{X}) \qquad (207)$$

Now we can still write an equation for the dynamics of the reduced density matrix, in ~~the~~ form

$$\bar{\rho}_s(\varphi,\varphi';t) = \int d\varphi_0 \int d\varphi_0' \, K(\varphi,\varphi';\varphi_0,\varphi_0';t,t_0)\, \bar{\rho}_s(\varphi_0,\varphi_0';t_0) \qquad (208)$$

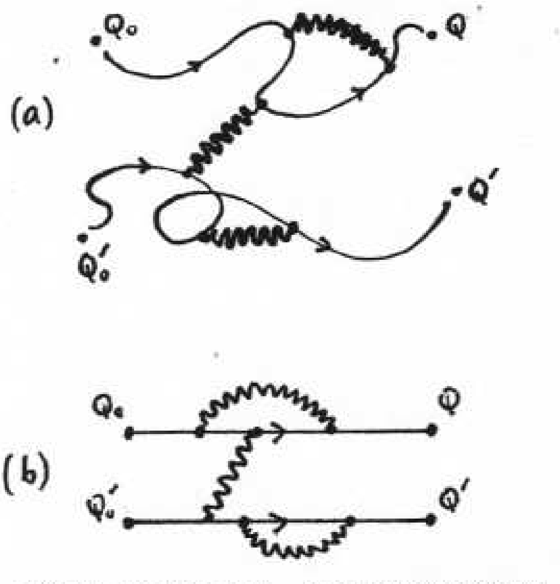
but now

$$K(\varphi,\varphi';\varphi_0,\varphi_0';t,t_0) = \int_{q(t_0)=\varphi_0}^{q(t)=\varphi} \mathcal{D}q(\tau) \int_{q'(\tau)=\varphi_0'}^{q'(t)=\varphi'} \mathcal{D}q'(\tau) \; \mathcal{F}[q,q']\, e^{i/\hbar(S_0[q]-S_0[q'])} \qquad (2$$

where the weighting functional $\mathcal{F}[q,q']$ assigns a weight to each pair of paths $(q(\tau), q(\tau'))$, over and above the phase weight already assigned to this pair by the the factor $\exp[i/\hbar(S_0[q]-S_0[q'])]$. This weighting functional was called the "influence functional" by its inventor Feynman, and it takes the form in general:

$$\mathcal{F}[q,q'] = \int \mathcal{D}X(\tau) \int \mathcal{D}X'(\tau)\, e^{i/\hbar(S_{int}[q,X]-S_{int}[q',X']+S_E[X]-S_E[X'])} \qquad (21$$

where the end-points of the functional integrals are not specified (strictly speaking we should integrate over these end-points, with some weight assigned to the integral, but we ignore this technicality here).



(a) PATH DESCRIPTION (b) FEYNMAN GRAPH

Again a diagrammatic interpretation is useful here. If we can understand the propagator of the environmental modes by a simple wavy line, then a perturbative expansion in the coupling gives the diagrams shown.

Note that the general form of $\mathcal{F}[q,q']$ will be

$$\mathcal{F}[q,q'] = e^{i/\hbar(\Phi[q,q'] + i\Gamma[q,q'])} \qquad (211)$$

ie., we get an extra "reactive" contribution to the phase for a pair of paths, and we also get a "decoherence" term $\Gamma[q,q']$, which suppresses some pairs of paths.

Note that none of what has been said so far has specified the nature of the environment, or the coupling to it. The simplest model that one can imagine for an environment is just a noise source - we can imagine the system coupling to a noise process $\xi(t)$, via a coupling

$$\mathcal{H}_{int}[Q,\xi] = gQ(t)\xi(t) \qquad (212)$$

and it is then fairly easy to show that the weighting function is

$$\mathcal{F}_{Noise}[Q,Q'] = \int \mathcal{D}\xi(t)\, P[\xi]\, e^{\frac{i}{\hbar}\int d\tau\, \xi(\tau)(Q(\tau)-Q'(\tau))} \qquad (213$$

where $P[\xi]$ assigns a weight to different "noise paths". However this kind of noise model is not usually adequate to describe real quantum environments.

(a) Path Integrals for Oscillator Baths : We now specialize to the case where the environment can be modelled by perturbative coupling to an oscillator bath environment. First, the general form of these models - one assumes that

$$\mathcal{H}_E = \frac{1}{2}\sum_{q=1}^{N}\left(\frac{p_q^2}{m_q} + m_q\omega_q^2 x_q^2\right) \qquad (214)$$

ie, a set of uncoupled oscillators ; and the coupling form is

$$\mathcal{H}_{int} = \sum_{q=1}^{N}\left[F_q(Q)\,x_q + G_q(P)\,p_q\right] \qquad (215)$$

which is often simplified to
$$\mathcal{H}_{int} \sim \sum_q c_q x_q Q \qquad (216)$$

As with any effective Hamiltonian we assume a UV cut-off Ω_0, and we also assume that the couplings are weak, ie., we assume that

$$|F_q|,\ |G_q|,\ |c_q| \sim O(1/N^{1/2}) \qquad (217)$$

where there N oscillators in the Hilbert space with energies $< \Omega_0$.

Physically such oscillators represent extended modes in the environment, and this means that the wave functions of these modes will have a normalisation factor $1/V^{1/2}$, where V is the size of the "box" containing the environmental modes. Since we have $N \propto V$, we get (217) automatically.

Under what circumstances can we justify such a model, with the environment represented by bosons, & with coupling linear in the oscillator coordinates? This question was addressed by Feynman & Vernon, & by Caldeira & Leggett. The main points are

- Suppose the original couplings $V(Q,X)$ in (207) are weak, ie suppose that

$$|V_{\alpha\beta}| \ll |\varepsilon_\alpha - \varepsilon_\beta| \qquad (218)$$

where
$$V_{\alpha\beta}(Q) = \int d^4X\, \phi_\alpha(\underline{X})\, V(Q,X)\, \phi_\beta(\underline{X}) \qquad (219)$$

and where $\{\mathcal{E}_\alpha\}$ are the exact eigenenergies of the original $\mathcal{H}_E(\underline{X})$. It then follows that the oscillators then correspond to all transitions between these states, with the oscillator energies being defined by

$$\omega_q \equiv (\mathcal{E}_\alpha - \mathcal{E}_\beta) \qquad (220)$$

for all such pairs (α, β). This was the Feynman-Vernon argument.

- However even if (218) is not satisfied, we can still define an oscillator bath model like (214) - (216), provided the oscillators are fast w.r.t. the system. This is done by using a Born-Oppenheimer type of argument. We first define ADIABATIC environmental states

$$\left.\begin{array}{ll} & \tilde{\phi}_\alpha(\underline{X}, Q) \\ \text{with energies} & \tilde{\mathcal{E}}_\alpha(Q) \end{array}\right\} \qquad (221)$$

which depend explicitly on Q; ie we include the effect of the coupling term. Now suppose Q moves on a timescale $T \gg \tilde{\mathcal{E}}_\alpha^{-1}$, so that its dynamics can only weakly excite the high-energy modes.

We can then define a Born-Oppenheimer "gauge potential" $A_{\alpha\beta}$, given by

$$iA_{\alpha\beta}(Q) = \int d^N X \; \tilde{\phi}_\alpha(\underline{X}, Q) \frac{\partial}{\partial Q} \tilde{\phi}_\beta(X, Q) \qquad (222)$$

and then we can make a mapping to an oscillator bath if

$$\left.\begin{array}{ll} & |A_{\alpha\beta}| \ll |\tilde{\mathcal{E}}_\alpha - \tilde{\mathcal{E}}_\beta| \\ \text{with} & \omega_q = (\tilde{\mathcal{E}}_\alpha - \tilde{\mathcal{E}}_\beta) \end{array}\right\} \qquad (223)$$

This is a much less restrictive condition than (218), and it explains why the mapping to an oscillator bath is so popular. Examples include

- Itinerant fermion baths, in 1, 2, & 3 dimensions (where the oscillators represent a combination of particle-hole pairs and collective modes
- Systems where there are also higher-order bosonic couplings in the environment (eg., multi-magnon couplings). These can be included as linear couplings to a new set of "canonically transformed" oscillators.
- A huge variety of bosonic extended modes (phonons, photons, magnons, spinons, etc) which may or may no couple strongly to the system.

We also see where the model fails - if there are many degenerate modes in the environment (so $\tilde{\mathcal{E}}_\alpha - \tilde{\mathcal{E}}_\beta = 0$), or if the modes are not extended.

(1) Form of Influence Functional : Without loss of generality we can actually get rid of the coupling $G_q(P)$ in (215), using a canonical transformation. The influence functional then takes the form

$$\mathcal{F}[Q,Q'] = \prod_{q=1}^{N} \int \mathcal{D}x_q(\tau) \int \mathcal{D}x_q(\tau') \, e^{i/\hbar \int d\tau \left[\frac{m_q}{2} \left(\dot{x}_q^2 - (x_q')^2 + \omega_q^2 (x_q^2 - (x_q')^2) \right) + (F_q x_q - F_q' x_q') \right]} \quad (224)$$

Now this functional integral is exactly solvable, as the exponent is a simple quadratic form in $X(t)$; we simply have a product of Gaussian integrals. The general result is actually more complicated than we want for the spin-boson model. Recall that the Hamiltonian for this model is

$$\mathcal{H}_{SB} = \left(\Delta_0 \hat{\tau}_x + \epsilon_0 \hat{\tau}_z \right) + \sum_q C_q x_q \hat{\tau} + \sum_q \left[\frac{p_q^2}{2m_q} + \frac{1}{2} m_q \omega_q^2 x_q^2 \right] \quad (225)$$

and that this either results from a spin-½ system coupled to an oscillator bath, or from a Hamiltonian like

$$\mathcal{H} = \frac{1}{2} M_0 \dot{Q}^2 + V(Q) + \sum_q V_q x_q Q + \sum_q \frac{1}{2} \left[\frac{p_q^2}{m_q} + m_q \omega_q^2 x_q^2 \right] \quad (226)$$

in which the potential $V(Q)$ truncates to a 2-level system at low energy. Thus the general coupling $F_q(Q) x_q$ in (224) is replaced by the bilinear coupling $V_q x_q Q$, and one finds that

$$\mathcal{F}[Q,Q'] = \exp\left\{ -\frac{1}{\hbar} \int_{t_0}^{t} d\tau_1 \int_{t_0}^{\tau_1} d\tau_2 \left(Q(\tau_1) - Q'(\tau_1) \right) \left(\mathcal{D}(\tau_1 - \tau_2) Q(\tau_2) - \mathcal{D}^*(\tau_1 - \tau_2) Q'(\tau_2) \right) \right. \quad (227)$$

which we can write in the form (211), with $\mathcal{F} = \exp\{ i/\hbar [\Phi + i\Gamma] \}$, where

$$\left. \begin{aligned} \Phi[Q,Q'] &= \int d\tau_1 \int d\tau_2 \, \mathrm{Im}\, \mathcal{D}(\tau_1 - \tau_2) \left(Q(\tau_1) - Q'(\tau_1) \right) \left(Q(\tau_2) + Q'(\tau_2) \right) \\ \Gamma[Q,Q'] &= \int d\tau_1 \int d\tau_2 \, \mathrm{Re}\, \mathcal{D}(\tau_1 - \tau_2) \left(Q(\tau_1) - Q'(\tau_1) \right) \left(Q(\tau_2) - Q'(\tau_2) \right) \end{aligned} \right\} \quad (228).$$

and where the bath propagator is

$$\mathcal{D}(\tau) = \frac{1}{2} \sum_q \frac{|V_q|^2}{m_q \omega_q} \left[e^{-i\omega_q \tau} + 2 \frac{\cos \omega_q \tau}{e^{\beta \omega_q} - 1} \right] \quad (229)$$

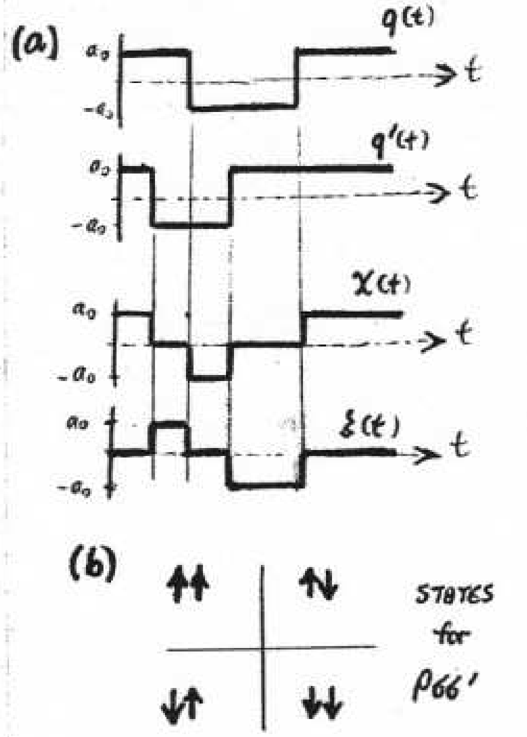
It is common to define a "Caldeira-Leggett" spectral function $J(\omega)$, defined as

$$J(\omega) = \frac{\pi}{2} \sum_q \frac{|V_q|^2}{m_q \omega_q} \delta(\omega - \omega_q) \quad (230)$$

which has the form of a (coupling constant)^2 × (density of states)/(energy denominator). Then we have

$$\left.\begin{aligned}\mathrm{Re}\, D(\tau) &= \int d\omega\, J(\omega) \cos\omega\tau \coth\left(\frac{\beta\omega}{2}\right) \\ \mathrm{Im}\, D(\tau) &= \int d\omega\, J(\omega) \sin\omega\tau\end{aligned}\right\} \quad (231)$$

(ii) Influence Functional for Spin-Boson Model: we have paths $Q(\tau) = \pm 1$ (ie., corresponding to $\tau_z = \pm 1$). Now we define the "diagonal" and "off-diagonal" variables



THE DENSITY MATRIX HOPS BETWEEN THE STATES SHOWN IN (b), ALONG THE PATHS SHOWN IN (a).

$$\left.\begin{aligned}\chi(\tau) &= \tfrac{1}{2}(Q(\tau) + Q'(\tau)) \\ \xi(\tau) &= \tfrac{1}{2}(Q(\tau) - Q'(\tau))\end{aligned}\right\} \quad (232)$$

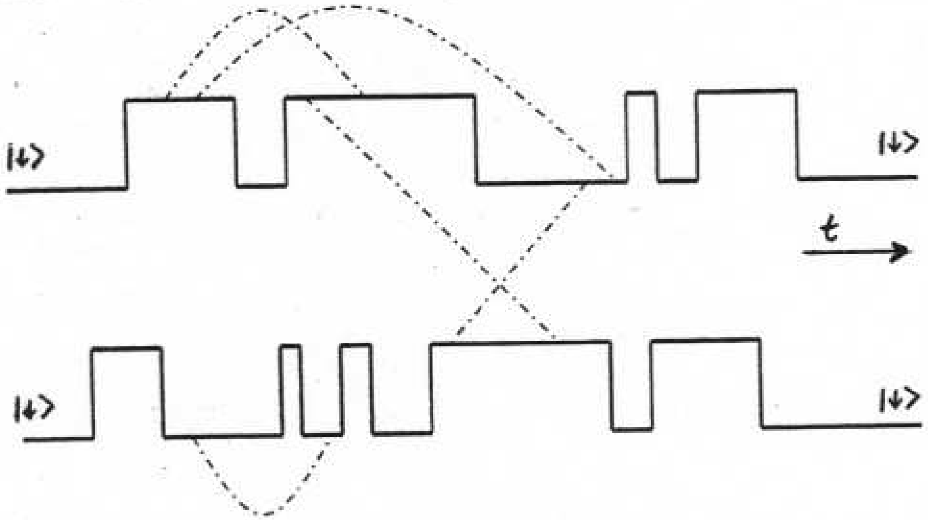
The reason for the names is that these variables give a nice representation of the states of the reduced density matrix for our central two-level system; defining this as $\bar{\rho}_{\sigma\sigma'}(t)$, we see that

$$\left.\begin{aligned}\chi(t) &\neq 0 \quad \text{for} \quad \rho_{\uparrow\uparrow}, \rho_{\downarrow\downarrow} \\ \xi(t) &\neq 0 \quad \text{for} \quad \rho_{\uparrow\downarrow}, \rho_{\downarrow\uparrow}\end{aligned}\right\} \quad (233)$$

The phase and decoherence functionals Φ and Γ now become

$$\left.\begin{aligned}\Phi(\chi,\xi) &= \int d\tau_1 \int d\tau_2\, \mathrm{Im}\, D(\tau_1 - \tau_2)\, \xi(\tau_1)\, \chi(\tau_2) \\ \Gamma(\xi) &= \int d\tau_1 \int d\tau_2\, \mathrm{Re}\, D(\tau_1 - \tau_2)\, \xi(\tau_1)\, \xi(\tau_2)\end{aligned}\right\} (234$$

We can interpret these formulae in the same way as we did above for general paths of the system. Interactions between the paths $Q(\tau)$ and $Q(\tau')$, or alternatively between the paths $\chi(\tau)$ and $\xi(\tau)$, are mediated by the bosonic modes, with interaction lines described by the propagator $D(\tau)$. The diagrams which then go into the path integral contain both "self-energy" terms (in which a path interacts with itself via a bath oscillator), and interactions between the 2 paths.



Note from (233) and (234 that the decoherence term arises from self-interactions of off-diagonal states of $\rho_{\sigma\sigma'}(t)$, ie., these off diagonal states are suppressed by the interactions. This decoherence functional involves $\mathrm{Re}\, D(\tau)$, and therefore the bath temp comes into the decoherence (compare (231)). In fact $\mathrm{Re}\, D(\tau)$ contains both spontaneous & stimulated emission / absorption processes

The mathematical study of the spin-boson dynamics has filled entire books, and several notable reviews. The first step is to expand the propagator over all possible combinations of flips at different times. This means generalizing expressions of the form (170) - (172) to pairs of paths, and then including the interactions. In other words, we write

$$K_{\sigma\sigma';\sigma_0\sigma_0'}(t) = \int \mathcal{D}Q(\tau) \int \mathcal{D}Q'(\tau)\, \mathcal{F}[Q,Q']\, A[Q]\, A^*[Q'] \qquad (235)$$

where $A[Q]$ takes the sum form as the sums in (170) - (172). To write out these sums is quite lengthy. In the following 2 subsections we will give a summary of results for 2 important special cases, and in both of these we employ results which are derived using a special approximation, the so-called "NIBA" (Non-Interacting Dilute Blip Approximation"), which works as follows: we take the general expansion of (235), which has the form

$$\left.\begin{aligned} K_{\sigma_2\sigma_2';\sigma_1\sigma_1'}(t,t_0) &= \sum_n{}' \sum_m{}' (-i\Delta_0)^{n+m}\, \mathcal{F}_{nm}(t-t_0) \\ \text{with} \quad \mathcal{F}_{nm}(t_2-t_1) &= \prod_{j=1}^{n} \prod_{k=1}^{m} \int_{t_0}^{t} dt_n \int_{t_0}^{t_n} dt_{n-1} \cdots \int_{t_0}^{t} dt_m \int_{t_0}^{t_m} dt_{m-1} \cdots\; f_{nm}(\chi(\tau), \xi(\tau)) \\ \text{where} \quad n &= \begin{matrix} \text{even if } \sigma_2 = \sigma_1 \\ \text{odd if } \sigma_2' = -\sigma_1 \end{matrix} \qquad m = \begin{matrix} \text{even if } \sigma_2' = \sigma_1' \\ \text{odd if } \sigma_2' = -\sigma_1' \end{matrix} \end{aligned}\right\} \quad (236)$$

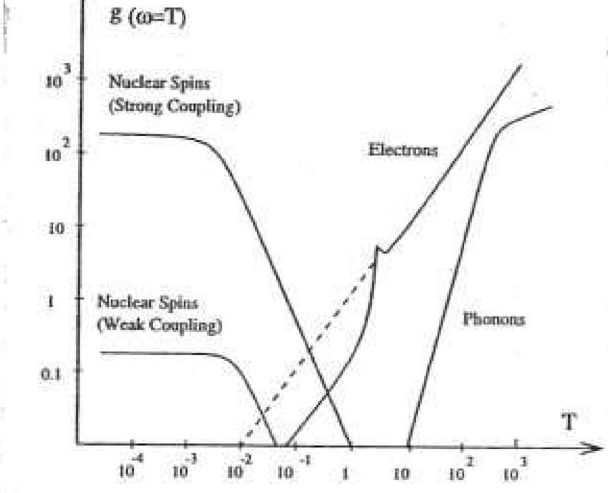
and where $f_{nm}(\chi, \xi)$ is a complicated function of the path, involving interactions between the states $\chi(\tau)$ and $\xi(\tau)$ at different times.

The NIBA then consists in ignoring all interactions except those between nearest-neighbour states. What this means is that off-diagonal states in $\rho_{\sigma\sigma'}(t)$ interact with their neighbouring diagonal states, but that is all. This simplifies the expressions enormously - and it can also be shown that the results are extremely accurate in most cases of interest. We do not give any formal details here, but those who are interested can look at the Appendix.

The final form of the dynamics depends crucially on what form is adapted for $J(\omega)$. In the diagram we see some typical forms. The Ohmic form is particularly relevant to fermionic environments, and as pointed out by Caldeira & Leggett, it yields Ohmic dissipation for the classical dynamics of the system at higher temperatures, once one is out of the low-T quantum regime.

One also has "superOhmic" forms for $J(\omega)$, which arise from bosonic excitations whose spectral weight increases at higher energies, because of increased phase space (e.g., phonons, photons, magnons, etc).

One can of course have more complex forms for $J(\omega)$, with gaps, and significant peak structure. In general $J(\omega, T)$ depends on the bath temperature.



Typical form for the dimensionless coupling $g(\omega, T)$, with $\omega = T$, between a mesoscopic system such as a superconductor or a nanomagnet, and various environmental modes. In this particular case we assume a three-dimensional system with nuclear spin energy scale $E_0 \sim 3 \times 10^3$ K, and a superconducting transition at $T \sim 2$ K.

(b) Results: Spin-Boson Dynamics - Ohmic Case

: We look here at a brief summary of the most important results for the dynamics here. It is convenient to look at a particular time correlation function which can be calculated from $\rho_{\sigma\sigma'}(t)$. Here we look at the function $P_{\uparrow\uparrow}(t)$, which can be evaluated directly from the propagator $K_{\uparrow\uparrow,\uparrow\uparrow}(t)$; it tells us the probability of finding the system in state $|\uparrow\rangle$, if at $t=0$ it was also in the state $|\uparrow\rangle$.

The Ohmic form of $J(\omega)$ is

$$J(\omega) = \eta\omega \qquad (\omega \ll \Omega_0) \tag{237}$$

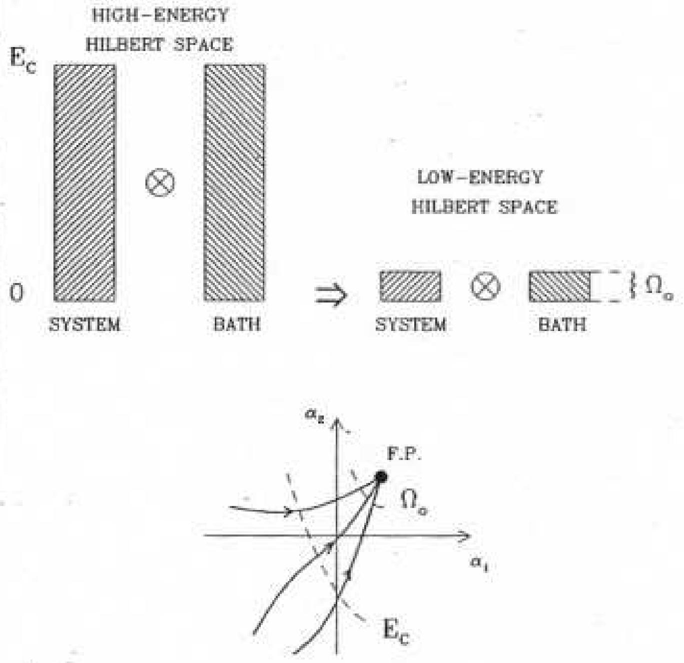
where it is assumed that there is a UV cut-off Ω_0 in the problem, so that all oscillators with $\omega \gg \Omega_0$ have already been eliminated from the problem (ie, incorporated into renormalized couplings, to the low-energy oscillators, and a renormalized pair of parameters ϵ_o, Δ_o. This is a very important point - we see that all the quantities Δ_o, ϵ_o, and $J(\omega, T)$ must depend implicitly on the UV cut-off adopted in the model. However, in a physically meaningful model, no physical quantity can depend on the value of Ω_0, provided we keep $\Omega_0 \gg$ all the energy scales in the model, ie., in this case, we keep

$$\Omega_0 \gg \Delta_o, \epsilon_o, kT \tag{238}.$$

Quite generally we expect the couplings in the renormalized Hamiltonian to "flow" as we change Ω_0 - this is a standard feature of RG theory, illustrated at left. We shall occasionally find it convenient to change Ω_0, both to verify this and to better understand the structure of the results.

To implement the UV-cut-off one can write $J(\omega)$ in various forms that include Ω_0; the one most commonly chosen is

$$J(\omega) = \eta\omega e^{-\omega/\Omega_0} \tag{239}$$



. The flow of a class of effective Hamiltonians describing a central system coupled to a background environment, in coupling constant space, as the UV cutoff in the joint Hilbert space is reduced from E_c to Ω_0. Here we show flow to a fixed point FP, in a simplified two-dimensional space of couplings α_1, α_2, but one may also have fixed lines or more complex topologies.

It is also convenient to define a dimensionless parameter:

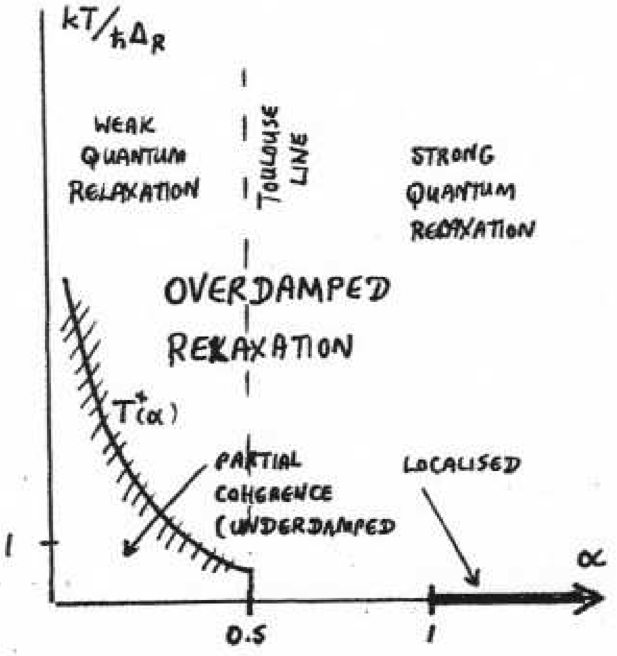
$$\alpha = \frac{a_o^2}{2\pi\hbar}\eta \tag{240}$$

which is invariant, like η, of Ω_0, provided (238) is satisfied.

In what follows we also assume that η, $J(\omega)$, and α are independent of T; this will not always be true in the application to real physical problems.

(i) Symmetric Case ($\epsilon_o = 0$): We have seen already (p. 46, and eqtns. (170) and (176)) how the central spin will behave when $\alpha = 0$; this case shows perfect coherence.

For finite α, the dynamics at $\epsilon_o = 0$ depends on α and on T. We can



PHASE DIAGRAM FOR OHMIC SPIN-BOSON SYSTEM. THE LINE $T^+(\alpha)$ IS A CROSSOVER BETWEEN PARTIAL DECOHERENCE & RELAXATION.

divide the "phase diagram" for the dynamics into separate regions, as shown at left. The system shows a "quantum phase transition" at $T=0$, at a value $\alpha = 1$. There is also another interesting transition at $\alpha = 1/2$, between partially coherent "quantum relaxation" when $\alpha < 1/2$, and completely incoherent relaxation when $1/2 \leq \alpha < 1$.

If we switch on the temperature, we also get various different regimes, as shown in the Figure. The solution simplifies very considerably along the line $\alpha = 1/2$; this is known as the "Toulouse line", since it was first noticed in the study of the anisotropic Kondo problem, which as we saw earlier (cf. eqn. (35)) can be mapped to the spin-boson model. Remarkably the transition between partially coherent and completely incoherent relaxation exists all along this line.

In what follows we summarize the results for the Ohmic case, as calculated using the **NIBA**. It turns the that the NIBA works out very well in the Ohmic case, indeed in parts of the phase diagram it is more of or less exact, to order Δ_0/Ω_0.

- <u>$T=0$, $0<\alpha<1/2$ (Partially coherent Q. Relaxation)</u>: In this case we have simple underdamped oscillations, according to the formula

$$P_{\uparrow\uparrow}(t, T=0) = A e^{-\gamma(\alpha)t}\cos\left(\tilde{\Delta}(\alpha)t\right) + \text{inc.} \tag{241}$$

where the renormalised tunneling amplitude is

$$\left.\begin{aligned} \tilde{\Delta}(\alpha) &= \left[\cos(\pi\alpha)\Gamma(1-2\alpha)\right]^{1/2(1-\alpha)}\cos\left(\frac{\pi}{2}\frac{\alpha}{1-\alpha}\right)\Delta_R \\ \Delta_R &= \Delta_0\left(\frac{\Delta_0}{\Omega_0}\right)^{\alpha/1-\alpha} \end{aligned}\right\} \tag{242}$$

and the damping rate is

$$\gamma(\alpha) = \left[\cos(\pi\alpha)\Gamma(1-2\alpha)\right]^{1/2(1-\alpha)}\sin\left(\frac{\pi}{2}\frac{\alpha}{1-\alpha}\right)\Delta_R \tag{243}$$

Note that the functions $\tilde{\Delta}(\alpha)$ and $\gamma(\alpha)$ depend explicitly on the ratio Δ_0/Ω_0, via the dependence of Δ_R on this ratio. At first glance this seems to completely contradict our assumption that the physical results cannot depend on the UV cut-off Ω_0. The solution to this paradox is that Δ_0 itself must depend on Ω_0, in such a way as to leave $\tilde{\Delta}(\alpha)$, $\gamma(\alpha)$, and Δ_R, independent of Ω_0. This is precisely what happens - in fact the parameter $\Delta_0(\Omega_0)$ is itself a mathematical construct, analogous to the "bare charge" and bare mass in QED. We discuss this point in more detail at the end of this sub-section. In any case from now on we expect everything to be a function of the physical parameter Δ_R, and/or $\tilde{\Delta}(\alpha)$.

- <u>$T=0$, $\frac{1}{2} < \alpha < 1$ (Incoherent Relaxation)</u> : In this regime the correlation function decays, after an initial transient, as a power law in time:

$$P_{pp}(t) \simeq \frac{1}{\pi} \sin 2\pi\alpha \, \Gamma(2-2\alpha) \frac{1}{(\tilde{\Delta}(\alpha) t)^{2(1-\alpha)}} \qquad (\tilde{\Delta}t \gg 1) \qquad (244)$$

The shorter-time transient behaviour is of non great interest, since it depends in real situations on the details of the state preparation. The result in (244) is nominally the dominant one, because it ignores other incoherent terms; but note that as $\alpha \to \frac{1}{2}$ from above, it disappears, and the results are more complicated. When $\alpha \geq 1$, at $T=0$, the system freezes: $P_{pp}(t) = 1$

- <u>Finite T, Coherent Dynamics ($T < T^*(\alpha)$)</u> : When we switch on the temperature, the system goes over to incoherent relaxation, except in a small region where the bath coupling is weak ($\alpha < \frac{1}{2}$), and the temperature is low ($T < T^*(\alpha)$). The crossover temperature $T^*(\alpha)$ is given by a rather complicated formula which is not quoted here - but a reasonable approximation is

$$kT^*(\alpha) \sim \hbar\Delta_r/\pi\alpha \qquad (\alpha < \tfrac{1}{2}) \qquad (245)$$

and in this regime we have the damped relaxation in (241), with

$$\left.\begin{aligned} \tilde{\Delta}_\alpha(T) &= \tilde{\Delta}(\alpha)\left[1+\alpha\left(\mathrm{Re}\,\psi\left(\frac{\hbar\tilde{\Delta}_\alpha}{2\pi kT}\right) - \ln\left(\frac{\hbar\tilde{\Delta}(\alpha)}{2\pi kT}\right)\right)\right] \\ \tilde{\gamma}_\alpha(T) &= \frac{\pi}{2}\alpha\tilde{\Delta}(\alpha)\coth\left(\frac{\hbar\tilde{\Delta}_\alpha}{2kT}\right) \end{aligned}\right\} \alpha \ll \tfrac{1}{2} \qquad (246)$$

with considerably more complicated formulae for larger α. (NB: $\psi(x)$ is the digamma fn.).

- <u>Finite T, Quantum Relaxation</u> : Over the rest of the finite T regime we have straightforward quantum relaxation, ie

$$P_{pp}(t) \sim e^{-\gamma_\alpha(T)t} \qquad (247)$$

where the T-dependent decay rate is given by

$$\left.\begin{aligned} \gamma_\alpha(T) &= \Delta_0\left(\frac{\Delta_0}{\Omega_0}\right)\frac{\Gamma^2(\alpha)}{\Gamma(2\alpha)}\left(\frac{2\pi kT}{\hbar\Omega_0}\right)^{2\alpha-1} \\ &\equiv \hbar\frac{\Gamma^2(\alpha)}{\Gamma(2\alpha)}\frac{\Delta_R^2}{kT}\left(\frac{2\pi kT}{\hbar\Delta_R}\right)^{2\alpha-1} \end{aligned}\right\} \qquad (248)$$

where the 2nd form is written in terms of the physical Δ_R. Note that $\gamma_\alpha(T)$ increases with T when $\alpha > \frac{1}{2}$, but decreases with T when $\alpha < \frac{1}{2}$.

- **Toulouse line ($\alpha = 1/2$)** : The relaxation rate, for arbitrary T, is given on the line $\alpha = \frac{1}{2}$, by

$$\left.\begin{aligned} \gamma_T \equiv \gamma(\alpha = 0.5) &= \frac{\pi}{2}\frac{\Delta_0^2}{\Omega_0} \\ &\equiv \frac{\pi}{2}\Delta_R \end{aligned}\right\} \text{ independent of } T \qquad (249)$$

This result can be derived in many different ways (eg, by fermionizing the system, or by a canonical transformation).

(ii) **General Case (Finite Bias)** : When the bias is finite, the system dynamics will always be relaxational, no matter what α or T may be - it is relaxing from the higher to the lower state, via a combination of spontaneous & stimulated processes.

The general result for the relaxation rate is

$$\gamma_\alpha(T,\epsilon_0) = 2\Delta_0\left(\frac{\Delta_0}{\Omega_0}\right)\left(\frac{2\pi kT}{\hbar\Omega_0}\right)^{2\alpha-1}\cosh\left(\frac{\epsilon_0}{2kT}\right)\frac{\left|\Gamma\left(\alpha + i\left(\frac{\epsilon_0}{2\pi kT}\right)\right)\right|^2}{\Gamma(2\alpha)} \qquad (250)$$

- which is fairly complicated! A useful limit arises when $\epsilon_0 \gg kT$, in which case (250) reduces to

$$\gamma_\alpha(\epsilon_0) = 2\pi\,\Delta_0\left(\frac{\Delta_0}{\Omega_0}\right)\frac{1}{\Gamma(2\alpha)}\left(\frac{\epsilon_0}{\hbar\Omega_0}\right)^{2\alpha-1} \qquad (251)$$

We can now summarize all of these results fairly simply. Except in the very restricted regime $\alpha < 1/2$, and $T < T^*(\alpha)$, where the system shows some damped coherent dynamics, the spin dynamics is quantum relaxational. When there is no bias on the system, this simply means that the system fluctuates between the states $|\uparrow\rangle$ and $|\downarrow\rangle$. At $T = 0$, when $\frac{1}{2} \leq \alpha < 1$, this happens entirely via quantum fluctuations, driven by the bath. At finite T, this happens through a combination of quantum & thermal fluctuations, with a crossover at $T^*(\alpha)$. For $\alpha \geq \frac{1}{2}$ this happens at any finite T, and so for $\alpha > 1/2$, thermal fluctuations drive the dynamics, at a rate which increases with T. For $\alpha < 1/2$, thermal fluctuations actually slow the dynamics down. The renormalisation of the physical tunneling matrix element to $\tilde{\Delta}(\alpha)$ arises because the oscillator bath wave-functions must readjust to the flipping of the central spin $\underline{\tau}$; for $\alpha > 1$, at $T = 0$, it renormalizes to zero.

(iii) **Renormalisation of $\tilde{\Delta}(\alpha)$: IR Catastrophe** : We now need to understand properly the renormalisation process, and show that the definition of Δ_R as the invariant renormalised quantity is correct. This means we need to understand how $\Delta(\Omega_0)$ scales with Ω_0.

In doing so we will get a simple understanding of the IR catastrophe in this problem, which is the same as that in the X-ray edge problem, the Kondo problem, and the Kosterlitz-Thouless transition.

Let us first ask - what is the physical meaning of $\Delta(\Omega_0) \equiv \Delta_0$? Consider what happens when we move the system from state $|\Uparrow\rangle$ to $|\Downarrow\rangle$. There is some "BARE" tunneling matrix element Δ_∞ for this, but now let's ask what happens to very high frequency oscillators, with $\omega_q > \Omega_0$, when we do this. This is answered by looking at the overlap between the oscillator states - these states adjust adiabatically to the change in qubit state. Formally we have states, when $kT \ll \hbar\Omega_0$, which look like

$$\left.\begin{aligned} |A\rangle &= |\Uparrow\rangle \prod_q |\phi_q^{(0)}(\uparrow)\rangle \; \theta(\omega_q - \Omega_0) \\ |B\rangle &= |\Downarrow\rangle \prod_q |\phi_q^{(0)}(\downarrow)\rangle \; \theta(\omega_q - \Omega_0) \end{aligned}\right\} \qquad (252)$$

and we are interested in the overlap integral between these states. The states $|\phi_q^{(0)}(\sigma)\rangle$, with $\sigma = \uparrow, \downarrow$, are the oscillator ground states, in the presence of the coupling $c_q x_q \hat{\tau}_z$ to the central spin; they are given by

$$|\phi_q^{(0)}(\sigma)\rangle = e^{i\sigma \frac{c_q}{\hbar m_q \omega_q^2} \hat{p}_q} \, |\phi_q^{(0)}(0)\rangle \equiv e^{-i\sigma \frac{c_q}{(2\hbar m_q \omega_q^3)^{1/2}} [b_q - b_q^\dagger]}$$

where $|\phi_q^{(0)}(0)\rangle$ is the undisplaced oscillator (ie., when the coupling $c_q = 0$). The overlap is now

$$\left.\begin{aligned} \Delta(\Omega_0) &= \Delta_\infty \langle A | \hat{\tau}_x | B \rangle \\ &= \Delta_\infty \prod_q \langle \phi_q^{(0)}(\uparrow) | \phi_q^{(0)}(\downarrow) \rangle \, \theta(\omega_q - \Omega_0) \\ &\equiv \Delta_\infty \exp\left\{ -\frac{a_0^2}{2\pi\hbar} \int_{\Omega_0}^{\infty} \frac{d\omega}{\omega^2} J(\omega) \right\} \end{aligned}\right\} \qquad (254)$$

Now suppose we want to renormalise down to a much lower frequency. From (254) we can see that by changing Ω_0 to $\Omega_0 - d\Omega_0$, we have the very simple lowest-order RG eqtn.

$$\frac{d \ln \Delta(\Omega_0)}{d \ln \Omega_0} = \frac{a_0^2}{2\pi\hbar} \frac{J(\Omega_0)}{\Omega_0} \qquad (255)$$

This is a very crude result (sometimes called "poor man's scaling"), but it will show us what we want to see. Suppose we have Ohmic coupling, so that

$$\frac{a_0^2}{2\pi\hbar} J(\omega) = \alpha\omega \qquad (256)$$

Now consider what happens when we try to scale down the UV cut-off, using (256) × (255). There are 2 possibilities - if we scale to a new cut-off $\Omega_0' < \Omega_0$, we have

$$\Delta(\Omega_0') = \Delta(\Omega_0) \left(\frac{\Omega_0'}{\Omega_0} \right)^{\alpha} \qquad (257)$$

and we see that if $\alpha \geq 1$, we get a scaling such that $\Delta_0(\Omega_c)$ decreases faster than Ω_c, so that

$$\tilde{\Delta}(\alpha) \longrightarrow 0 \qquad (\alpha \geq 1) \qquad (258)$$

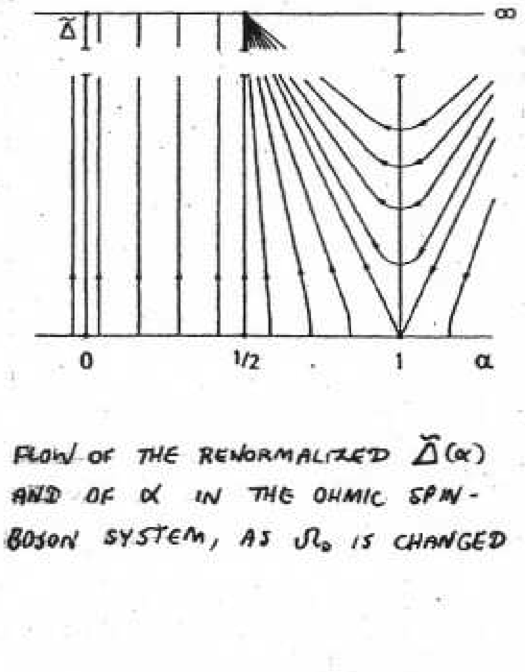
Suppose now we have $\alpha < 1$. From (257) we can write a self-consistent eqtn by asking what happens if we try to scale Ω_0' all the way down to $\Delta(\Omega_0')$; if there is a solution Δ_R, then it must be given by

$$\Delta_R = \Delta(\Omega_0)\left(\frac{\Delta_R}{\Omega_0}\right)^{\alpha} \qquad (\alpha < 1) \qquad (259)$$

which simply means that

$$\Delta_R = \Delta_0\left(\frac{\Delta_0}{\Omega_0}\right)^{\frac{\alpha}{1-\alpha}} \qquad (260)$$

which is precisely what we found. A more accurate RG calculation would not give Δ_R, but instead give $\tilde{\Delta}(\alpha)$, but this involves much more sophisticated methods. These are nevertheless interesting, because the scaling here is the same as that in the anisotropic Kondo model, the quantum Sine-Gordon model, & in fact many other models - it is usually called Kosterlitz-Thouless scaling. In this RG formulation one recognises that both α and $\tilde{\Delta}(\alpha)$ can in principle scale as we vary the UV cut-off. In the anisotropic Kondo model this corresponds to a scaling of J_z and $J_{\parallel}$ with UV cut-off. There are 2 fixed points for the scaling. One the one hand the system can flow to a "localised" fixed point, with $\tilde{\Delta} = 0$. On the other hand it can flow to a delocalised fixed point, where tunneling is still possible. In any realistic physical situation the frequency scale we look at (which will not be at the fixed point) will be set by the physical situation itself.



FLOW OF THE RENORMALIZED $\tilde{\Delta}(\alpha)$ AND OF α IN THE OHMIC SPIN-BOSON SYSTEM, AS Ω_0 IS CHANGED

Further details of this are rather complex, and are discussed in the literature. They are also illuminated by the various exact solutions of models like this one, which can be related to a variety of 1-d problems, which in the case of Ohmic dissipation have conformal symmetry.

(c) Results for Spin Dynamics: SuperOhmic Case : Let's briefly consider the scaling argument given above, but this time for "superOhmic" dissipation. SuperOhmic couplings are typically described by the form

$$\left.\begin{aligned} \frac{a_0^2}{2\pi\hbar} J(\omega) &\sim g\left(\frac{\omega}{\Omega_0}\right)^{m} e^{-\omega/\Omega_0} \equiv \bar{g}\,\frac{\omega^{m}}{\Omega_0^{m-1}}\, e^{-\omega/\Omega_0} \\ \bar{g} &= g/\Omega_0 \end{aligned}\right\} \qquad (261)$$

so that the dimensionless coupling $\bar{g}(\Omega_0)$ (again a function of the UV cutoff) tells us how strong the coupling actually is. The same kind of simple scaling argument as above now tells us that the tunneling matrix element will renormalize to a finite value no matter how large is $\bar{g}$, provided the exponent m in $J(\omega)$ is > 1. This renormalisation is easily found to be

$$\left.\begin{aligned} \tilde{\Delta}(\bar{g}) &\sim \Delta_0 e^{-F} \\ F &= \frac{a_0^2}{2\pi\hbar}\int_0^{\Omega_0} d\omega\, \frac{J(\omega)}{\omega^2} \sim \bar{g}\,\frac{\Omega_0^{m}}{n-1} \end{aligned}\right\} \quad (262)$$

where F is usually known as the "Franck-Condon" or "Debye-Waller" factor.

In the discussion of scaling for the Ohmic case, we restricted our discussion to $T=0$. If one works at finite T, things are modified somewhat, and they are here too. In fact the Debye-Waller factor at finite T becomes

$$F(T) = \frac{a_0^2}{2\pi\hbar}\int_0^{\Omega_0} d\omega\, \frac{J(\omega)}{\omega^2}\coth\left(\frac{\hbar\omega}{2kT}\right) \quad (263)$$

Whether one uses this function is a matter of taste - one could equally adapt the integral to $\int_{kT}^{\Omega_0} d\omega$, so as to restrict the renormalisation to be for energies $> kT$. However we will use $F(T)$ for convenience in what follows.

(i) <u>The Symmetric Case ($\epsilon_0 = 0$)</u> : The results for this problem turn out to depend in an important way on what m is. When $m > 2$, one always gets damped oscillations, but when $1 < m < 2$, the oscillations can be suppressed. Note that in 3 dimensions, the exponent m for diagonal coupling to phonons or photons is $m = 3$. We separate the 2 discussions accordingly.

- <u>The case $s > 2$</u> : For this case we have results that can be stated fairly quickly, either for the case of zero temperature or for $T \neq 0$. We get damped oscillations:

$$P_{\uparrow\uparrow}(t) \sim e^{-\gamma t}\cos(\tilde{\Delta}t) \quad (264)$$

where as above

$$\Delta(\bar{g}, T) = \Delta_0 e^{-F(T)} \quad (265)$$

and the damping is

$$\left.\begin{aligned} \gamma(\bar{g}, T) &= \frac{a_0^2}{4\hbar} J(\tilde{\Delta})\coth\left(\frac{\hbar\tilde{\Delta}(T)}{2kT}\right) \\ &= \frac{\pi}{2}\bar{g}\,\frac{\tilde{\Delta}^{M}}{\Omega_0^{M-1}}\coth\left(\frac{\hbar\tilde{\Delta}}{2kT}\right) \end{aligned}\right\} \quad (266)$$

- <u>The case $1 < s < 2$</u> : The dynamics here are somewhat reminiscent of the weakly-coupled Ohmic case (when $\alpha < 1/2$). We find that there is a crossover temperature, given by

$$kT^*(\bar{g}) = \hbar\left(\frac{a_0^2}{2\pi\hbar}\right)\frac{\tilde{\Delta}^2}{g}\left(\frac{\Omega_0}{\tilde{\Delta}}\right)^{m} \quad (267)$$

Above this temperature the dynamics is damped, whereas below it we get underdamped oscillations. The expressions are complicated & I don't give them here.

(ii) <u>The Biased Case ($\epsilon_0 \neq 0$)</u> : Here the results are pretty simple, and apply for the whole range $m > 1$. We get a straightforward decay, of the form

$$P_{\uparrow\uparrow}(t) \sim e^{-\gamma t} \tag{268}$$

where now the finite-T decay rate is given by

$$\left.\begin{aligned} \gamma(\bar{g};\epsilon_0,T) &= \frac{a_0^2}{2\hbar}\left(\frac{\hbar\tilde{\Delta}}{\tilde{E}_0}\right)^2 J\left(\frac{\tilde{E}_0}{\hbar}\right)\coth\left(\frac{\tilde{E}_0}{2kT}\right) \\ &\equiv \pi\bar{g}\,\frac{E_0^{m}}{\Omega_0^{m-1}}\left(\frac{\hbar\tilde{\Delta}}{E_0}\right)^2\coth\left(\frac{\tilde{E}_0}{2kT}\right) \end{aligned}\right\} \tag{269}$$

where as before E_0 is the total level-splitting :

$$\tilde{E}_0^2 = \hat{\Delta}^2 + \epsilon_0^2 \tag{270}$$

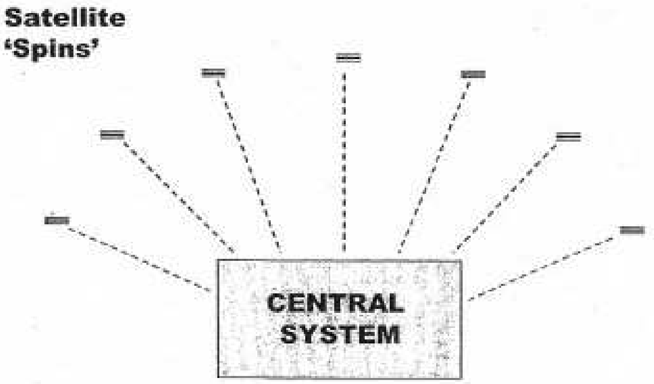
From the eqtns (264) - (270) we see that in fact it is not so hard to understand the superOhmic case. What matters is the spectral density $J(\omega)$ at the energy $\tilde{E}_0$ which is relevant to the bath-mediated transitions (noting that $\tilde{E}_0 \to \tilde{\Delta}$ in zero bias). The factor of $(\hbar\tilde{\Delta}/E_0)^2$ in (269) comes from the fact that the overlap between the exact states $|+\rangle$ and $|-\rangle$, separated by $\tilde{E}_0$, and the states $|\uparrow\rangle$ and/or $|\downarrow\rangle$, is reduced by this factor.

A.2.3 :- <u>DYNAMICS OF THE CENTRAL SPIN + SPIN BATH</u>

We now turn to that class of models in which a central system is coupled to a set of <u>discrete</u> environmental modes, which may not now be represented as oscillators. In this case one can also give general arguments, which tell us when we may model the environment in this way, and what form the couplings must take. Suppose we return to our general Hamiltonian form

$$\left.\begin{aligned} \mathcal{H} = \mathcal{H}_0(P,Q) &+ \mathcal{H}_{int}(P,Q;X,\dot{X}) \\ &+ \mathcal{H}_{env}(X,\dot{X}) \end{aligned}\right\} \tag{271}$$

(cf (207) and (214)-(216)), but now we assume that in the energy range of interest, the environmental modes must be represented as states in a discrete Hilbert space. We will write



GENERAL FORM OF A MODEL IN WHICH A CENTRAL QUANTUM SYSTEM IS COUPLED TO A SET OF "BATH" OR "SATELLITE" SPINS.

$$\mathcal{H}_{env} = \sum_k \mathbf{h}_k \cdot \boldsymbol{\sigma}_k + \sum_{kk'} V_{kk'}^{\alpha\beta}\sigma_k^{\alpha}\sigma_{k'}^{\beta}$$ (272

where the $\{\underline{\sigma}_k\}$ are a set of "2-level systems". A fairly general coupling form for this coupling is

$$\mathcal{H}_{int} = \sum_k^N \underline{F}_k(Q,P)\cdot\hat{\underline{\sigma}}_k \tag{273}$$

Now let us consider what physically reasonable assumptions we can make about the couplings in (272) & (273).

– The first assumption we make is that because the bath degrees of freedom are localised, they hardly see each other, so that the $V_{kk'}$ are weak – in fact we assume that

$$|V_{kk'}| \ll |\underline{F}_k(P,Q)| \quad \forall\, k,k' \tag{274}$$

and often we have $\qquad |V_{kk'}| \ll |\underline{h}_k| \qquad (275)$

as well. If the $\{\underline{\sigma}_k\}$ do represent local degrees of freedom, interacting locally with some quantum system, then we notice that there is no particular reason to assume that $|\underline{F}_k|$ even depends on the number N of bath spins, and certainly no reason to assume a dependence like $|\underline{F}_k| \sim O(N^{-1/2})$. Thus the $\underline{F}_k$ can be quite large, whereas the $V_{kk'}$ typically fall off like dipolar interactions with distance $|\underline{r}_k - \underline{r}_{k'}|$.

Note that if neither (274) nor (275) were satisfied, we could actually make an oscillator bath – the $V_{kk'}$ would allow the formation of "spin waves" from the bath spins. However the large $|\underline{h}_k|$ will simply localize these, as will the $\underline{F}_k$ if the system is stationary.

Thus we see that in one respect the spin bath is almost completely opposite to the oscillator bath. Instead of the intrinsic energies dominating over the external couplings (for the oscillator bath, $|\omega_q| \gg |c_q|$), we have exactly the opposite – we have $|V_{kk'}| \ll |\underline{F}_k|$ for the spin bath. Thus in this sense the spin bath is partially *slaved* to the central system.

Actually there is another energy scale in the problem. Suppose that the characteristic timescale for changes in the central system coordinate Q is a time T, so that

$$\left|\frac{\partial_t \underline{F}_k}{\underline{F}_k}\right| T \sim O(1). \tag{276}$$

and now define the "adiabaticity parameter" $\qquad u_k = \dfrac{1}{|\underline{F}_k| T} \sim \left|\dfrac{\partial_t \underline{F}_k}{\underline{F}_k^2}\right| \qquad (277)$

Then we have 2 limits:

$$\left.\begin{array}{ll} u_k \ll 1 & \text{slow "adiabatic" limit} \\ u_k \gg 1 & \text{fast "sudden" limit} \end{array}\right\} \tag{278}$$

In the slow limit, the bath spins follow the system very easily, whereas in the fast limit, Q changes too rapidly for the bath spins to track it.

Let us see how these considerations work in practise for the coupling of a qubit to a spin bath. There are many examples one could take here. These include (i) a magnetic molecule or magnetic cluster coupled to nuclear spins (ii) a superconducting SQUID coupled to defects (TLS's) in the junction and substrate, as well as to paramagnetic and nuclear spins (iii) A quantum dot qubit coupled to charge traps (also TLS's) and to nuclear spins (iv) ions in an ion trap coupled to charge fluctuators in the electrodes; etc We take one example in particular

<u>Example of Truncation to Central Spin model</u> : Let us consider again our tunneling giant spin, & couple it to nuclear spins in the surrounding environment. Recall that we are interested in a system with effective Hamiltonian

$$\mathcal{H}_{eff}(S_0; I_k) = \mathcal{H}_o(\underline{S}_o) + \mathcal{H}_{int}(\underline{S}_o, \{\underline{I}_k\}) + S_E(\{I_k\}) \qquad (279,$$

where we

$$\mathcal{H}_o(\underline{S}_o) = \left(-DS_z^2 + ES_x^2\right) - g\mu_B \underline{S}_o \cdot \underline{H}_o \qquad (280)$$

$$\left.\begin{aligned} \mathcal{H}_{int}(S_o, \{I_k\}) &= \sum_k \tilde{A}_k^{\alpha\beta} S_0^\alpha I_k^\beta \\ &\equiv \sum_j \sum_k A_{jk}^{\alpha\beta} s_j^\alpha I_k^\beta \end{aligned}\right\} \qquad (281,$$

$$\mathcal{H}_E(\{\underline{I}_k\}) = \sum_k \left[-g_k^N \mu_N \underline{I}_k \cdot \underline{H}_o + Q_k^{\alpha\beta} I_k^\alpha I_k^\beta\right] + \sum_{kk'} V_{kk'}^{\alpha\beta} I_k^\alpha I_{k'}^\beta \qquad (282)$$

ie., we assume a biaxial giant spin, along with a set of nuclear spins (cf eqtn (87)). To simplify what follows, let's make the following approximations:

$$Q_k^{\alpha\beta} = 0 \quad \& \quad \hat{\underline{I}}_k \rightarrow \hat{\underline{\sigma}}_k \quad (\text{spin } \tfrac{1}{2}). \qquad (283)$$

Now consider the form that the tunneling action must take. We have

$$L_{eff}(\underline{S}_o, \{\underline{I}_k\}) = L_o(\underline{S}_o) + L_{int}(\underline{S}_o, \{\ _k\}) + L_E(\{\ _k\}) \qquad (234)$$

where

$$\left.\begin{aligned} L_o(\underline{n}, \dot{\underline{n}}) &= iS\dot{\theta}\phi \sin\theta - \mathcal{H}_o(S\underline{n}) + g\mu_B S_o \underline{n} \cdot \underline{H}_o \\ L_{int}(\underline{n}, \dot{\underline{n}}; \underline{\sigma}_k, \dot{\sigma}_k) &= \tfrac{1}{2} S_0 \sum_k \tilde{A}_k^{\alpha\beta} n^\alpha \sigma_k^\beta \\ L_E(\sigma_k, \dot{\sigma}_k) &= \frac{i}{2}\sum_k \dot{\theta}_k \phi_k \sin\theta_k + g_k^N \mu_N \underline{\sigma}_k \cdot H_o - \sum_{kk'} V_{kk'}^{\alpha\beta} \sigma_k^\alpha \sigma_{k'}^\beta \end{aligned}\right\} (235)$$

where $\underline{\sigma}_k(t)$ is considered to be a classical vector for the moment (representing the coherent state for the nuclear spin).

Now the key to deriving an effective Hamiltonian for the qubit is to notice that each nuclear spin is actually adding a very weak field

$$\underline{b}_k^\alpha = \tfrac{1}{2} S_o \tilde{A}_k^{\alpha\beta} \sigma^\beta \qquad (236)$$

acting on the <u>central</u> spin - we assume realistically that $|\underline{b}_k| << D/S,\ E/S$. Thus we can treat this small field as a small perturbation on the central spin system. What is the effect of this on the dynamics of $\underline{S}_0$? This is a fairly straightforward problem to solve. Suppose we go back to our simple tunneling problem, with now a Lagrangian

$$\left.\begin{aligned} \tilde{L}_0(n,\dot{n}) &= -iS_0\dot{\theta}\phi\sin\theta - \mathcal{H}_0(n) + \underline{n}\cdot\underline{b}_k \\ \tilde{\mathcal{H}}_0(S\underline{n}) &= S^2D\left[\sin^2\theta + E/D\,\sin^2\theta\sin^2\phi\right] \end{aligned}\right\} \qquad (236)$$

ie., the same as the problem we already solved but with an extra term

$$\delta L_b = \left(b_k^x\sin\theta\cos\phi + b_k^y\sin\theta\sin\phi + b_k^z\cos\theta\right) \qquad (287)$$

in the system. We will be concerned therefore with only small changes to the tunneling paths, and to the action along these paths. We again fix ϕ to be close to 0 or π, and keep only terms $\sim O(\underline{b}_k)$. This immediately gives the generalization of eqtn (187):

$$L_0 \rightarrow \left[\frac{\dot{\theta}^2}{4D} + S^2E\sin^2\theta\right] + \left(b_k^x\sin\theta + i\frac{\dot{\theta}}{SE}b_k^y + b_k^z\cos\theta\right) \qquad (288)$$

To this lowest order, we may evaluate the change in action of the tunneling system caused by the field as

$$\left.\begin{aligned} \delta S_b^{(\eta)} &= \int d\tau\, \delta L_b^{(\eta)}(n,\dot{n}) \\ &= \frac{\pi}{\omega_0}\eta\,\underline{b}_k\cdot\left(\hat{\underline{x}} + if\left(\tfrac{D}{E}\right)\hat{\underline{y}}\right) \end{aligned}\right\} \qquad (289)$$

where, for example, in the regime where $D \ll E$, we have $f(D/E) = (D/E)^{1/2}$.
If we now substitute in (236), we see that we can write, for a <u>stationary</u> nuclear spin $\underline{\sigma}_k$, that

$$\delta S^{(\eta)} = i\eta\,\underline{\alpha}_k\cdot\underline{\sigma}_k \qquad (290)$$

with components

$$\alpha_k^\beta = S_0\left(-iA_k^{x\beta},\ f(D/E)A^{y\beta}\right) \qquad (281)$$

But now let us notice that (i) δS in (284) is just the action of a constant field $(\hat{x} + if(D/E)\hat{y})$ on $\underline{b}_k$; and (ii) that this addition to the action is simply equivalent to a new spin-dependent phase - ie, we can write (cf. (190)):

$$\left.\begin{aligned} &\tilde{\Phi}_0^{(\eta)} \quad \Phi_0^{(\eta)} + \delta\Phi_k^{(\eta)} \\ &\delta\Phi_k^{(\eta)} = i\eta\,\underline{\alpha}_k\cdot\underline{\sigma}_k \end{aligned}\right\} \qquad (292)$$

and a new tunneling amplitude

$$\left.\begin{aligned}\tilde{\Delta}(\underline{S}_0;\{\sigma_k\}) &= \omega_0 \sum_{\eta=\pm}\left(\frac{2}{\pi}\mathrm{Re}\,\tilde{\Phi}^{(\eta)}\right)e^{-\tilde{\Phi}^{(\eta)}} \\ &= \frac{1}{2}\tilde{\Delta}_0(S_0)\sum_{\eta=\pm} e^{i\eta[\pi S_0 + \sum_k \underline{\alpha}_k\cdot\underline{\sigma}_k]}\end{aligned}\right\} \quad (293)$$

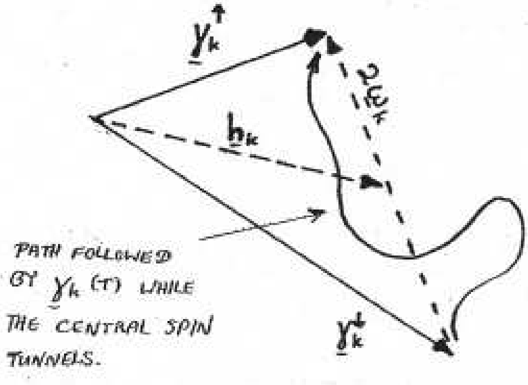
Now let us recall what our goal was here – we want to derive an effective Hamiltonian for the system, in which we have truncated to the 2 lowest "qubit" levels for $\underline{S}_0$. But in fact the above derivation has already told us what the non-diagonal flipping term must be – it is just

$$\mathcal{H}_{eff}(\underline{\tau},\{\sigma_k\}) = \frac{1}{2}\tilde{\Delta}_0\left[\hat{\tau}_+ e^{i[\pi S_0 + \sum_k \underline{\alpha}_k\cdot\hat{\underline{\sigma}}_k]} + H.c.\right] \quad (294)$$

in which now $\hat{\sigma}_k$ and $\hat{\tau}$ are <u>operators</u>. However we see there must be other terms as well. Eqtn (294) describes all terms associated with $\hat{\tau}_\pm$ in the effective Hamiltonian, ie, associated with the rapid transitions between states $|\Uparrow\rangle$ and $|\Downarrow\rangle$; but what about the long "quiescent" periods when it is in one or other of these states. This is a much easier question to answer – we simply ask what is the energy of the system in these states. It is convenient to do this as follows; define the field $\underline{\gamma}_k$, with components

$$\left.\begin{aligned}\gamma_k^\beta &= \sum_j A_{jk}^{\alpha\beta} s_j^\alpha - \mu_N g_k^N H_0^\beta \\ &\equiv S_0^\alpha \tilde{A}_k^{\alpha\beta} - \mu_N g_k^N H_0^\beta\end{aligned}\right\} \quad (295)$$

as the field acting on the k-th bath spin from the central spin. Now $\underline{S}_0$ is shunting back and forth between the 2 coherent states $|\underline{n}^\uparrow\rangle$ and $|\underline{n}^\downarrow\rangle$ so that $\underline{\gamma}_k$ is shunting between corresponding vectors $\underline{\gamma}_k^\uparrow$ and $\underline{\gamma}_k^\downarrow$, as $\hat{\tau}_z$ goes from ± 1,



$$\left.\begin{aligned}\underline{\omega}_k &= \frac{1}{2}(\underline{\gamma}_k^\uparrow - \underline{\gamma}_k^\downarrow) \\ \underline{h}_k &= \frac{1}{2}(\underline{\gamma}_k^\uparrow + \underline{\gamma}_k^\downarrow)\end{aligned}\right\} \quad (296)$$

We can then write the diagonal part of the Hamiltonian as

$$\mathcal{H}_{eff}^D = \sum_k(\underline{h}_k + \underline{\omega}_k\hat{\tau}_z)\cdot\underline{I}_k \quad (297)$$

where

$$\left.\begin{aligned}\underline{\omega}_k\cdot\underline{I}_k &= \frac{1}{2}S_0 A_k^{\alpha\beta}(n^\uparrow - n^\downarrow)\cdot I_k^\beta \\ \underline{h}_k\cdot I_k &= \frac{1}{2}S_0 A_k^{\alpha\beta}(n_\alpha^\uparrow + n_\alpha^\downarrow)\cdot I_k^\beta - \mu_N g_k \underline{H}_0\cdot I_k\end{aligned}\right\} \quad (298)$$

Finally, we have the term $\sum_{kk'} V_{kk'}^{\alpha\beta} I_k^\alpha I_{k'}^\beta$, which is entirely unaltered by these higher-energy renormalisations.

We can now write the final derived form of the central spin model. For a bath described by a set $\{\underline{\sigma}_k\}$ of 2-level systems, we have

$$\left.\begin{aligned} \mathcal{H}_{eff}(\tau,\{\sigma_k\}) = \; & \tfrac{1}{2}\tilde{\Delta}_0 \left\{ \hat{\tau}_+ e^{i(\pi S_0 + \sum_k \alpha_k \cdot \underline{\sigma}_k]} + H.c. \right\} + \epsilon_0 \hat{\tau}_z \\ & + \sum_k (\underline{h}_k + \underline{\omega}_k \hat{\tau}_z) \cdot \underline{\sigma}_k + \sum_{kk'} V_{kk'} \sigma_k^\alpha \sigma_{k'}^\beta \end{aligned}\right\} \quad (299)$$

and for a bath of modes $\{\underline{I}_k\}$ where $|\underline{I}_k| > \frac{1}{2}$, one can show that we must (a) replace $\underline{\sigma}_k$ by $\underline{I}_k$ everywhere, and (ii) add in the term $\sum_k Q_k^{\alpha\beta} I_k^\alpha I_{k'}^\beta$ that we previously dropped.

It is useful to note that the general method used here to derive the low-E effective Hamiltonian is fairly simple to state. It can be enumerated in 2 steps:

(i) <u>Non-diagonal terms</u>: We start off by defining a "transfer matrix" as

$$\hat{T}_\pm^k \,|\underline{\sigma}_k\rangle = e^{-\frac{i}{\hbar}\int_-^+ d\tau\, \mathcal{H}_{int}} \,|\underline{\sigma}_k\rangle \qquad (300)$$

acting on the bath spins, where $\mathcal{H}_{int}$ is the interaction between the central system (whatever it may be) and the bath spin $\underline{\sigma}_k$, and we assume the central spin follows and instanton path over the time integral. Now we can always write

$$\int_-^+ d\tau\, \mathcal{H}_{int}(Q,\{\sigma_k\}) = \phi_k + \underline{\alpha}_k \cdot \underline{\sigma}_k \qquad (301)$$

for a spin-½ system, where both ϕ_k and $\underline{\alpha}_k$ are complex. In the development above we have ignored ϕ_k; its real part will slightly renormalize the phase of the tunneling system, and its imaginary part renormalizes the tunneling matrix element. If we now exponentiate (301) along the various tunneling paths, we get (294) for the tunneling giant spin

(ii) <u>Diagonal Terms</u>: These are found by writing down all terms in the energy of the system when the qubit is sitting in one of the 2 states $|\Uparrow\rangle$ or $|\Downarrow\rangle$.

(a) <u>Path Integrals for Spin Baths</u>

: Our experience with influence functionals for the oscillator bath makes this an easier exercise than before. We want to functionally integrate

$$\mathcal{F}[Q,Q'] = \int \mathcal{D}\underline{\sigma}_k(\tau) \int \mathcal{D}\underline{\sigma}_k(\tau')\, e^{\frac{i}{\hbar}(S_{int}[\,,\sigma_k] - S_{int}[\,;\sigma_k'] + S_E[\sigma_k] - S_E[\sigma_k'])} \qquad (302)$$

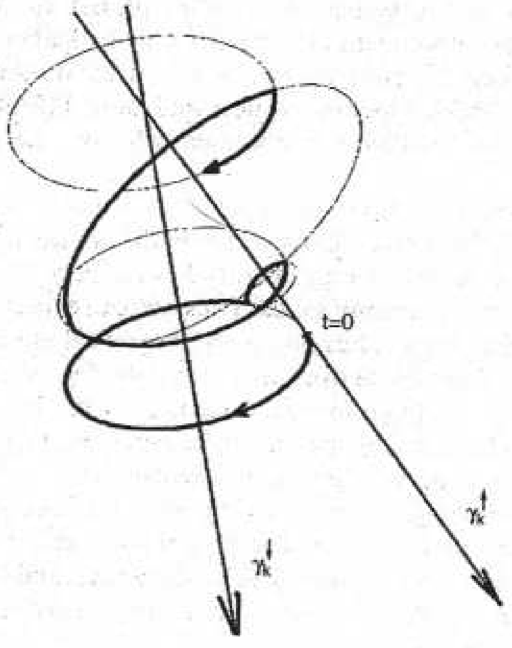
where the terms are written as (here A_k is the monopole vector potential):

$$\left.\begin{aligned} S_{int}[Q,\underline{\sigma}_k] &= -\int d\tau \sum_k \underline{F}_k(P,Q)\cdot\underline{\sigma}_k(\tau) \\ S_E[\underline{\sigma}_k,\dot{\underline{\sigma}}_k] &= \int d\tau \sum_k \left[\tfrac{1}{2}\underline{A}_k\cdot\dot{\underline{\sigma}}_k + g_k^N\mu_N \underline{H}_0\cdot\underline{\sigma}_k - \sum_{kk'} V_{kk'}^{\alpha\beta}\sigma_k^\alpha\sigma_{k'}^\beta\right] \end{aligned}\right\} \quad (303)$$

with an obvious generalisation to a set $\{\underline{I}_k\}$ of bath spins. In the case of a qubit this reduces to a functional $\mathcal{F}[\tau_z,\tau_z']$, with a form given for the effective Hamiltonian (299) by

$$\left.\begin{aligned} S_{int}[\tau_z,\underline{\sigma}_k] &= -\int d\tau\left\{\tfrac{1}{2}\Delta_0\left[\tau_+ e^{i[\pi S_0+\sum_k \underline{\alpha}_k\cdot\underline{\sigma}_k]} + H.c.\right] + \hat{\tau}_z\,\omega_k\cdot\underline{\sigma}_k(\tau)\right\} \\ S_E[\underline{\sigma}_k,\dot{\underline{\sigma}}_k] &= \int d\tau \sum_k \left[\tfrac{1}{2}\underline{A}_k\cdot\dot{\underline{\sigma}}_k - \underline{h}_k\cdot\sigma_k(\tau)\right] - \sum_{kk'} V_{kk'}^{\alpha\beta}\sigma_k^\alpha(\tau)\sigma_{k'}^\beta(\tau) \end{aligned}\right\} (304$$

Now let's look at these physically. The interaction term is simply describing the effect on $\underline{\sigma}_k(\tau)$ of a time-dependent field $\underline{F}_k(P,Q)$, while under the influence of the "potential" terms $\underline{H}_0$ and $V_{kk'}$. In the case of the qubit the paths followed by the central system are simple, and we can get a rather precise picture of what is going on.



In the Figure at left we see the effect we expect on $\underline{\sigma}_k(\tau)$ from the 2 most important terms in (304), ie., we look at the effect of

$$\mathcal{H}(\sigma_k) = (\underline{h}_k + \hat{\tau}_z\underline{\omega}_k)\cdot\underline{\sigma}_k \qquad (305)$$

on the spin σ_k. Essentially we are asking what is the effect of a field $\gamma_k(\tau)$ on $\sigma_k(\tau)$, when $\gamma_k(\tau)$ is flipping back & forth between 2 orientations as shown in the Figure, between $\gamma_k^{\uparrow}$ and $\gamma_k^{\downarrow}$, where

$$\underline{\gamma}_k^{\sigma} = \underline{h}_k + \sigma\underline{\omega}_k \qquad (306).$$

The key physical point here is that each time the central spin flips, the k-th bath spin must begin precessing anew, around the new field. We see that in doing so its dynamics must become entangled with that of the central spin.

The effect of the much smaller terms $\underline{\alpha}_k\cdot\sigma_k$ and $V_{kk'}^{\alpha\beta}\sigma_k^\alpha\sigma_{k'}^\beta$ can be handled perturbatively once the main effect from (305) has been dealt with.

In fact a proper derivation and discussion of $\mathcal{F}[Q,Q']$ is quite lengthy, and so we will not go through it here, since our main goal is the understanding ~~of~~ the central spin model. Therefore in what follows we simply describe how things work for this system (next page).

(i) <u>Evaluation of Path Integral for Central Spin System</u> : What we will do here is just give, without proof (but giving some sketchy arguments) the results for the general form of the path integral averaging for this system.

We begin with the most important terms in the problem, contained in the effective Hamiltonian (303). We begin by classifying the environmental spin bath states. How we do this depends on the ratio $|h_k/\omega_k|$; let us assume to be specific that the "external" fields $\{h_k\}$ are small. Then, for a given state of the qubit ($|\Uparrow\rangle$ or $|\Downarrow\rangle$), we classify the states according to their "polarisation group" M, defined by

$$M = \sum_k \sigma_k^z \qquad (307)$$

Then all states of the bath with the same M are in this polarisation group. We have a density of states

$$G_M(\epsilon) = \sum_{\{\sigma_k\}} \delta\Big(\sum_k \sigma_k^z - M\Big)\ \delta\Big(\epsilon - \sum_k \omega_k \sigma_k^z\Big) \qquad (308)$$

for the M-th polarisation group, and

$$W(\epsilon) = \sum_M G_M(\epsilon) \qquad (309)$$

for the total bath. In these equations we have defined the axis of quantization for each σ_k to be parallel to ω_k ; and the sum in (308) over the $\{\sigma_k\}$ is over all configurations (all 2^N of them) in the spin bath.

What these densities of states look like depends very much on the system. However in the most obvious case they will be Gaussian distributed, ie., we will have the forms

$$G_M(\epsilon) = C_N^{\frac{1}{2}(N+M)}\, g_M(\epsilon) \qquad (310)$$

where $\bar{g}_M(\epsilon)$ is the normalized Gaussian

$$\bar{g}_M(\epsilon) = \left(\frac{2}{\pi \Gamma_M^2}\right)^{\frac{1}{2}} e^{-2\epsilon^2/\Gamma_M^2} \qquad (311)$$

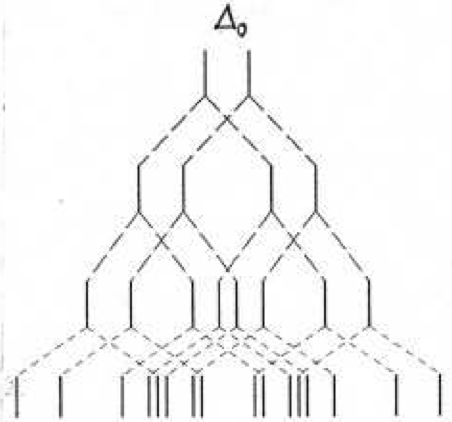
and

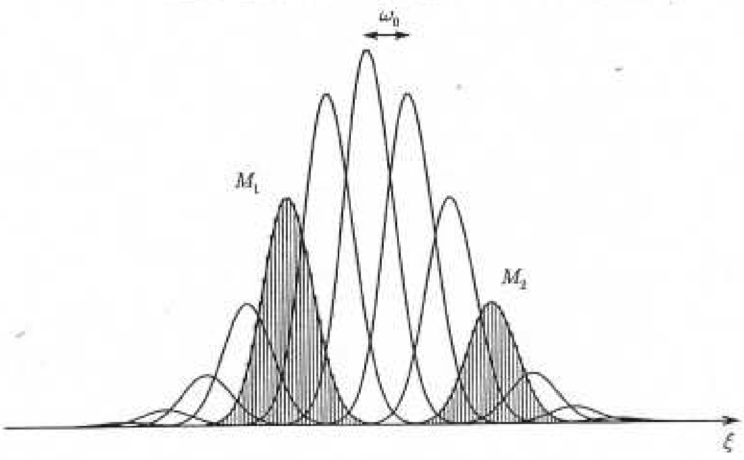
$$C_n^m = \frac{n!}{m!\,(n-m)!} \qquad (312)$$

Then we have

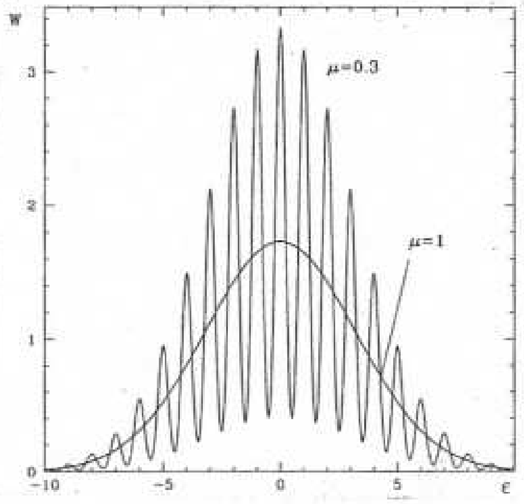
$$W(\epsilon) = 2^N\, \bar{w}(\epsilon) \qquad (313)$$

where $\bar{w}(\epsilon)$ is also normalised. The results are shown at left. We note that if the width





Polarisation Groups in the Spin Bath.
Density of states $W(\xi)$ of the $\prod_k(2I_k+1)$ of nuclear states in a magnetic qubit, which form an envelope of half-width E_0 (with $E_0^2 = \sum_k(\omega_k^{\parallel})^2$) around each qubit state. We assume $k = 1, 2, ..N$ (ie., N nuclear spins in each qubit), and zero applied field. The multiplet can be subdivided into "polarisation groups" , where the M-th polarisation group has a net spin $M = \sum_k I_k^z$ along the easy z-axis. These groups are separated by the mean value $\omega_0 = =< \omega_k^{\parallel} >$. Transitions between polarisation groups, which change the total spin projection, can only be mediated by T_1 processes coming from interaction with the environment, or stimulated by the qubit dynamics itself.



Γ_M of each polarisation group is small enough, then a "Gaussian toothcomb" structure will be visible in $W(\epsilon)$. We can define a parameter μ, given by

$$\mu_M = \Gamma_M / \omega_0 \qquad (314)$$

where $\omega_0 = \bar{\omega}_k$ is the mean value of ω_k; since typically Γ_M will not depend too strongly on M, at least in the central regions of $W(\epsilon)$, μ_M is to a first approximation independent of M. When the number N of bath spins is large, we have typically $\mu \gg 1$, and then

$$\tilde{W}(\epsilon) \xrightarrow[\mu \gg 1]{} \left(\frac{2}{\pi E_0^2}\right)^{1/2} e^{-2\epsilon^2/E_0^2} \qquad (315)$$

Notice that each time the qubit flips, the energies of all the bath spins reverse - this is rather important in what follows.

We now want to look at the different kinds of process involved in the path integral for the qubit, which will contribute to the influence functional $\mathcal{F}[\tau_z, \tau_z']$, and to the time evolution of $\rho_{\alpha\alpha'}(t)$. Let us consider what sort of processes will appear in the paths that appear in the sum over paths for transition amplitudes.

We note that if we begin by ignoring the non-diagonal couplings to the bath, embodied in the parameter $\underline{\alpha}_k$ in (301), then we only have to deal with processes coupling the qubit to the bath during the long intermediate diagonal periods between instanton qubit flips. This is what we did in our study of the spin-boson problem, in which we assumed only diagonal couplings.

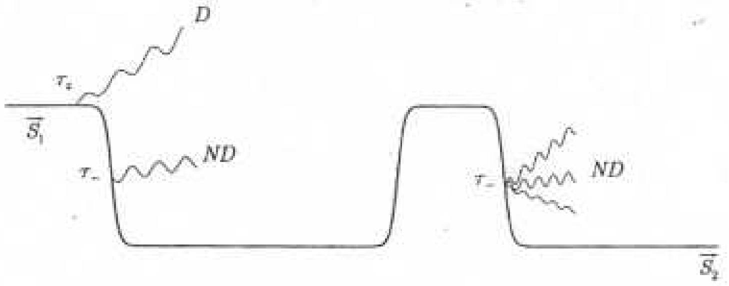


Fig. 9. A typical tunneling path for a qubit (shown here for a magnetic qubit, tunneling between states $|S_1\rangle$ and $|S_2\rangle$). These paths include coupling to the environment, shown as interaction vertices. Diagonal couplings (D) are defined as couplings to $\hat{\tau}_z$ (ie., taking place while the qubit is in one of the "stationary states" $|\Uparrow\rangle$ or $|\Downarrow\rangle$), and non-diagonal couplings (ND), occurring during transitions between the two, are to $\hat{\tau}_\pm$. The wavy lines represent either oscillator or spin bath modes.

We therefore begin by looking at the structure of the path integral for the Hamiltonian

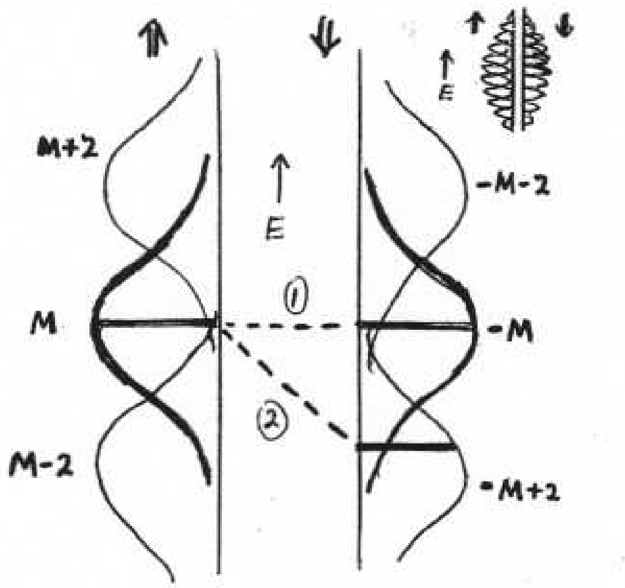
$$\mathcal{H}_D = (\Delta_0 \hat{\tau}_x + \epsilon_0 \hat{\tau}_z) + \sum_{k=1}^{N} (\underline{h}_k + \hat{\tau}_z \underline{\omega}_k) \cdot \hat{\underline{\sigma}}_k \qquad (316)$$

where, as noted above, we define the axes of quantization for the $\underline{\sigma}_k$ so that $\underline{\omega}_k = \hat{z}\omega_k$; and we begin by assuming

$$|\underline{h}_k| \ll |\underline{\omega}_k| \qquad (317)$$

For pedagogical purposes it is simplest to assume that $\epsilon_0 = 0$ in what follows; the generalisation to finite ϵ_0 is simple.

Consider now what happens to the combined qubit-spin bath system when the qubit flips. On page 71 we saw an intuitive picture of this - now let's do it formally. First note that if the bath starts off in polarisation group M_0, so that it has an energy $\sim \omega_0 M_0$ (with a spread Γ_M), then in order for energy to be conserved, the polarisation group must change to $-M$; we note that energy of a given spin bath state changes sign when the qubit flips. This situation is shown in the Figure below. (note that if $\Gamma_M > \omega_0$, then the final bath state may be in a polarisation group M' which may not be $-M_0$, but it will be close to it).



TRANSITIONS BETWEEN STATES IN THE SPIN BATH, WHEN THE CENTRAL QUBIT FLIPS IN EXTERNAL BIAS $\epsilon_0 = 0$. THE BATH POLARISATION GROUP DENSITIES OF STATES ARE SHOWN FOR QUBIT STATES $|\Uparrow\rangle$ & $|\Downarrow\rangle$ ALONG WITH A TRANSITION ① THAT CONSERVES BATH ENERGY (TRANSITION ② DOES NOT).

To implement this constraint we define a projection operator

$$\left.\begin{aligned}\hat{\Pi}_M &= \delta\left(M - \sum_k \hat{\sigma}_k^z\right) \\ &\equiv \int_0^{2\pi} \frac{d\xi}{2\pi}\, e^{i\xi\left(M - \sum_k \sigma_k^z\right)}\end{aligned}\right\} \quad (318)$$

and we introduce the unitary operator $\hat{U}_k$ defined by

$$\left.\begin{aligned}|\sigma_k^{out}\rangle &= \hat{U}_k\, |\sigma_k^{in}\rangle \\ &= e^{-i\beta_k \hat{\sigma}_k^x}\, |\sigma_k^{in}\rangle\end{aligned}\right\} \quad (319)$$

with

$$\cos 2\beta_k = -\frac{\underline{\gamma}_k^{\uparrow} \cdot \underline{\gamma}_k^{\downarrow}}{|\underline{\gamma}_k^{\uparrow}|\,|\underline{\gamma}_k^{\downarrow}|} \quad (320)$$

Since we are assuming $|\underline{h}_k / \underline{\omega}_k| \ll 1$, The field γ_k flips through nearly 180° when τ_z flips - it misses doing so by the small angle β_k, so that we can rewrite (320) as

$$\sin \beta_k \sim \beta_k \sim |\underline{h}_k / \underline{\omega}_k| \quad (321)$$

The operator $\hat{U}_k$ then rotates the basis for σ_k from the initial direction of γ_k, before the flip to that after the flip. But we notice that it also acts on σ_k to make it precess - this is precisely the process depicted in the picture on p. 71.

Consider now the amplitude for the transition

$$|\Uparrow, M_0 ; t=0\rangle \longrightarrow |\Uparrow, M-2M ; t\rangle \quad (322)$$

in which the bath polarisation group changes by $2M$. We can write this as

$$G_{\Uparrow\Uparrow}^{M_0, M}(t) = \sum_{n=0}^{\infty} \frac{(-i\Delta_0 t)^{2n}}{(2n)!} \prod_{j=1}^{2n} \int \frac{d\xi_j}{2\pi}\, e^{-iM_0 \sum_j \xi_j}\, e^{2iM \sum_{j'}^{odd} \xi_{j'}}\, \hat{T}_{2M} \quad (323)$$

where

$$\hat{T}_{2n} = e^{i\xi_{2n} \sum_k \sigma_k^z}\, \hat{U}^{+} e^{i\xi_{2n-1} \sum_k \sigma_k^z}\, \hat{U} \ldots \hat{U}^{+} e^{i\xi_1 \sum_k \sigma_k^z}\, \hat{U} \quad (324)$$

and the total unitary operator

$$\hat{U} = \prod_k \hat{U}_k \equiv e^{-i \sum_k \beta_k \hat{\sigma}_k^x} \quad (325)$$

The structure of this expansion reflects precisely the physical precession process – the operator U_k intervenes between each instanton flip, and the projection operator, in the form (318), forces spins to stay in a given polarisation group during these periods. The time dynamics of the density matrix is given by an obvious generalisation of this:

$$\bar{\rho}_{\sigma\sigma'}(t) = \sum_M W_M \bar{\rho}^M_{\sigma\sigma'}(t) \qquad (326)$$

where W_M is the probability that the system starts in the M-th polarisation group, and $\rho^M_{\sigma\sigma'}$ is the density matrix for a system where the bath is constrained to stay in this group. One finds that, for example:

$$\left.\begin{aligned} \bar{\rho}^M_{\uparrow\uparrow}(t) = \sum_n^\infty \sum_m^\infty \frac{(-i\Delta_0 t)^{2(n+m)}}{(2n)!\,(2m)!} \prod_{i=1}^{2n} \prod_{j=1}^{2m} \int \frac{d\xi_i}{2\pi} \int \frac{d\xi_j'}{2\pi} \times \\ \times\, e^{iM\left(\sum_{i=1}^{2n} \xi_i - \sum_{j=1}^{2m} \xi_j' - \sum_{i\in odd} \xi_i + \sum_{j\in odd} \xi_j'\right)} \left\langle T^+_{2m}\, T_{2n} \right\rangle \end{aligned}\right\} \quad (327)$$

where the average $\langle \cdots \rangle$ is taken over the bath spins, at some temperature. In the next sub-section we will see what this leads to.

Let us now consider the effect of the non-diagonal term in the effective Hamiltonian. To deal with this it is convenient to isolate the non-diagonal term, and study the Hamiltonian

$$\mathcal{H}_{ND} = \Delta_0 \left\{ \hat{\tau}_+ e^{i\sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k} + H.c. \right\} = \Delta_0 \hat{\tau}_x \cos\left(\sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k\right) \qquad (328)$$

The question we address is – how to do path integrals with this Hamiltonian. More generally we would like to address non-diagonal terms like that in (299), of the form

$$\left.\begin{aligned} \mathcal{H}_{ND} &= \Delta_0 \left[\hat{\tau}_+ e^{-i[\Phi_0 + \sum_k \underline{\alpha}_k \cdot \hat{\underline{\sigma}}_k]} + H.c \right] \\ &\equiv \Delta_0 \hat{\tau}_x \cos\left(\Phi_0 + \sum_k \underline{\alpha}_k \cdot \hat{\underline{\sigma}}_k\right) \end{aligned}\right\} \qquad (329)$$

Now consider the amplitude $A^{\beta\alpha}_{\Uparrow\Uparrow}$ for the system to go from state $|\Uparrow; \prod_k \sigma^\alpha_k\rangle$ to state $|\Uparrow; \prod_k \sigma^\beta_k\rangle$, ie.,

$$A^{\beta\alpha}_{\Uparrow\Uparrow} = \langle \Uparrow, \prod_k \sigma^\beta_k | e^{-i\mathcal{H}_{ND} t} | \Uparrow; \prod_k \sigma^\alpha_k \rangle \qquad (330)$$

In the usual way we expand in flips, to get for $\mathcal{H}_{ND}$ in (329):

$$\begin{aligned} A^{\beta\alpha}_{\Uparrow\Uparrow}(t) &= \langle \prod_k \sigma^\beta_k | \sum_{n=0}^\infty \int_0^t dt_{2n} \cdots \int_0^{t_2} dt_1 \left(-i\Delta_0 \cos\left[\Phi_0 + \sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k\right]\right)^{2n} | \prod_k \sigma^\alpha_k \rangle \\ &\equiv \sum_{n=0}^\infty \frac{(-i\Delta_0 t)^{2n}}{(2n)!} \langle \beta | \cos^{2n}\left(\Phi_0 + \sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k\right) | \alpha \rangle \end{aligned} \qquad (331)$$

To calculate the density matrix we now assume some initial spin bath density matrix, which may or may not be thermal, and get the obvious generalisation of (331); thus, e.g.,

$$\bar{\rho}_{\uparrow\uparrow}(t) = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{(i\Delta_0 t)^{2(n+m)}}{(2n)!\,(2m)!} \left\langle \cos^{2(n+m)}\left[\Phi_0 + \sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k\right] \right\rangle \qquad (332)$$

with the average over the bath. How we now proceed depends on what this average is assumed to be - let us here make the specific assumption that

$$\rho_{Bath}(\{\underline{\sigma}_k\}) = \prod_{k=1}^{N} \begin{pmatrix} p_k^{\uparrow} & 0 \\ 0 & p_k^{\downarrow} \end{pmatrix} \qquad (333)$$

and moreover we will assume that

$$p_k^{\uparrow} = p_k^{\downarrow} = \tfrac{1}{2} \quad \forall\ k \qquad (334)$$

ie., we assume that the temperature kT is high compared to energies of interest in the problem (which eventually will mean that $kT \gg |\underline{\omega}_k|, |\underline{h}_k|$).

Now we expand the cosine as

$$\cos^{2(n+m)}\left[\Phi_0 + \sum_k \underline{\alpha}_k \cdot \hat{\underline{\sigma}}_k\right] = \frac{1}{2^{n+m}} \sum_{\mu_\ell = \pm} e^{i\sum_{\ell=1}^{2(n+m)} \mu_\ell (\Phi_0 + \sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k)} \qquad (335)$$

Now if we assume (334), we can immediately write

$$\prod_k \left\langle e^{i\sum_\ell \mu_\ell \underline{\alpha}_k \cdot \underline{\sigma}_k} \right\rangle \xrightarrow[\text{high } T]{} \prod_k \cos\left(\sum_\ell \mu_\ell |\underline{\alpha}_k|\right) \qquad (336)$$

which can be verified by expanding the exponential $e^{i\underline{\alpha}_k \cdot \underline{\sigma}_k} = \cos(\underline{\alpha}_k \cdot \underline{\sigma}_k) + i\sin(\underline{\alpha}_k \cdot \underline{\sigma}_k)$; only the cosine term contributes). If we now write

$$\nu = \frac{1}{2}\sum_{\ell=1}^{2(n+m)} \mu_\ell \quad (\mu_\ell = \pm) \qquad (337)$$

then we can write

$$\left\langle \cos^{2(n+m)}\left[\Phi_0 + \sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k\right] \right\rangle = \sum_{\mu_\ell}^{\pm} \int_0^{2\pi} \frac{d\varphi}{2\pi} \sum_{\nu=-\infty}^{\infty} e^{i\nu\Phi_0}\, e^{-i\varphi(\nu - \sum_{\ell=1}^{2(n+m)} \mu_\ell)} \frac{1}{2^{2(n+m)}} \prod_k \cos(2\nu|\underline{\alpha}_k|)$$

$$= \int_0^{2\pi} \frac{d\varphi}{2\pi} \sum_{\nu=-\infty}^{\infty} F_\nu\, e^{i\nu(\Phi_0 - \nu)} \cos^{2(n+m)}\varphi \qquad (338)$$

where the last step uses the identity

$$(\cos\varphi)^{2M} = \frac{1}{2^M} \sum_{\mu_\ell}^{\pm} e^{i\varphi \sum_{\ell=1}^{2M} \mu_\ell} \qquad (339)$$

and we define

$$F_\nu = \prod_{k=1}^{N} \cos(2\nu|\underline{\alpha}_k|) \qquad (340)$$

We now substitute (338) back into back into our expression (332) for $\bar{\rho}_{\uparrow\uparrow}(t)$, to get

$$\bar{\rho}_{\uparrow\uparrow}(t) = \sum_{\nu=-\infty}^{\infty} \int_0^{2\pi} \frac{d\varphi}{2\pi} F_\nu \, e^{i\nu(\Phi_0-\varphi)} \rho^{(0)}_{\uparrow\uparrow}(t;\Delta_0(\varphi)) \qquad (341)$$

where $\rho^0_{\uparrow\uparrow}(t,\Delta_0(\varphi))$ is the propagator for a FREE SPIN, but with the renormalized tunneling matrix element

$$\Delta_0(\varphi) = \Delta_0 \cos\varphi \qquad (342)$$

ie.,

$$\bar{\rho}^{(0)}_{\uparrow\uparrow}(t,\Delta_0(\varphi)) = \cos^2(\Delta_0(\varphi)t) \qquad (343)$$

(NB: to get (341) we use the obvious identity

$$\sum_n \sum_m \frac{(i\Delta_0 t)^{2(n+m)}}{(2n)!\,(2m)!} (\cos\varphi)^{2(n+m)} = \cos^2[\Delta_0 t \cos\varphi] \qquad (344)$$

This almost concludes our discussion of how to deal with the main terms in the effective Hamiltonian (299). We see that in fact the ways of dealing with the diagonal & non-diagonal terms are not so different from each other, & both use straightforward instanton expansions. The resemblance between the two becomes even more striking if we actually evaluate the sums in (327). We then find that

$$\left.\begin{aligned} \bar{\rho}^M_{\uparrow\uparrow}(t) &= \int_0^\infty dy \, e^{-y} \rho^{(0)}_{\uparrow\uparrow}(t;\tilde{\Delta}_M(y)) \\ \text{where} \quad \Delta_M(y) &= \Delta_0 J_M(2\sqrt{\kappa y}) \end{aligned}\right\} \qquad (345)$$

where J_M is a Bessel fn., and

$$e^{-\kappa} = \prod_k |\cos\beta_k| \qquad (346)$$

Thus we see that for both the diagonal and non-diagonal interactions, we can reduce the evaluation of $\bar{\rho}_{\uparrow\uparrow}(t)$ to the evaluation of the free qubit propagator, but using a modified tunneling matrix element which contains a phase which is then averaged over. In the case of the non-diagonal terms this is a phase φ which is actually a topological phase for the bath spin. In the case of the diagonal terms this phase is imaginary, of form iy, and hence we get the form in (345). It is interesting that one may deal with the opposite limit from (317), where instead

$$|\underline{h}_k/\underline{\omega}_k| \gg 1 \qquad (347)$$

in exactly the same way as above - the only change is that β_k now represents the ratio

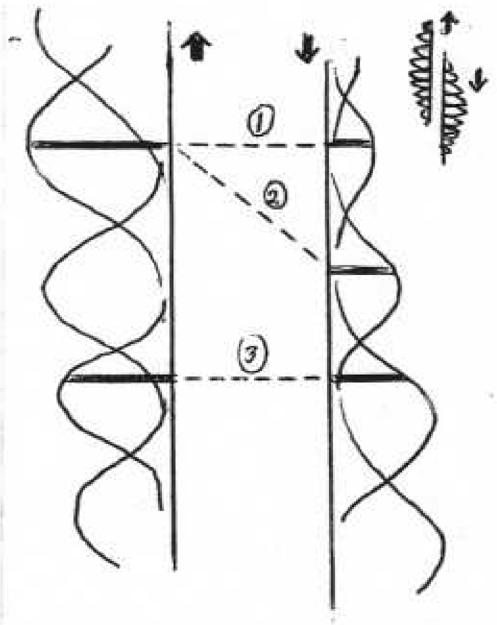
$$\beta_k \sim |\underline{\omega}_k/\underline{h}_k| \ll 1 \qquad (348)$$

and all the formulae go through as before.

There are just 2 things left to do to make the discussion complete. First we need to deal with the effect of the bias term $\epsilon_0\hat{\tau}_z$ in (299), and deal in general with the average over different bath states of differing energies. Second, we have to deal with the small interaction $V_{kk'}^{\alpha\beta}$ between the bath spins.

The effect of an energy bias is simple to handle. Notice that the total field now acting on the qubit is not ϵ_0, but in fact

$$\tilde{E}(t) = \epsilon_0 + \sum_k \omega_k \sigma_k^z(t) \qquad (349)$$

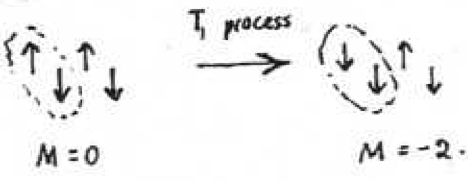


TRANSITIONS BETWEEN SPIN BATH STATES WHEN THERE IS A FINITE BIAS ϵ_0 ON THE QUBIT. TRANSITIONS ① AND ③ CONSERVE ENERGY, BUT TRANSITION ② DOES NOT.

In any realistic situation the initial state of the spin bath will be some complicated mixture, which may or may not be a thermal mixture. This means we must average over the bath states in getting our answer. If we do this, we must simply average the answers we have above. This means integrating over ξ, and summing over M. This average is ~~straight~~forward – it is specified formally below.

The effect of the small interaction term $V_{kk'}^{\alpha\beta}$ is rather less obvious. The first question to ask is why we care about it at all – after is many orders of magnitude smaller than $\underline{h}_k$ or $\underline{\omega}_k$. The reason is that it drives fluctuations in the spin bath which are very different in nature from the transitions that are caused by the combination of $\underline{h}_k$ and $\underline{\omega}_k$. To see this lets consider a pair of bath spins, as shown below. There are 2 kinds of interesting process, which in NMR language are called T_1 and T_2 processes.

T_1 processes involve a change in the total polarisation of the system along the axis of quantization – in the figure this means a change in polarisation group from $M = 0$ to $M = 2$. On the other hand T_2 processes do not change M; all we have is some kind of "pair flip" process. In NMR or ESR these processes have names, viz:



T_1 = longitudinal relaxation time
T_2 = transverse relaxation time

Now imagine that we have N bath spins, so that these processes are happening all over the bath – the probability for a given spin to take part in a T_1 or T_2 processes is T_1^{-1} or T_2^{-1} respectively, per unit time, and there are NT_1^{-1} and NT_2^{-1} such processes occuring per second throughout the bath.

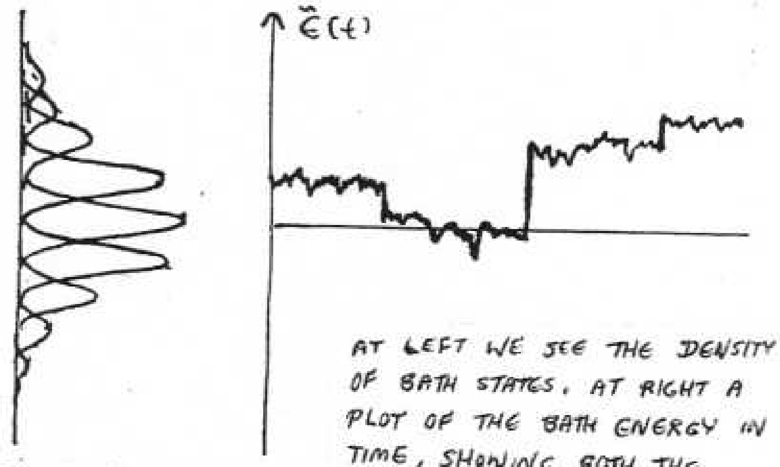
This suggests the following approximation to deal with this "fluctuational dynamics" in the spin bath. Let us write that

$$\sum_{kk'} V_{kk'}^{\alpha\beta} \sigma_k^{\alpha} \sigma_{k'}^{\beta} \sim \sum_k \underline{\xi}_k \cdot \sigma_k \qquad (350)$$

where $\underline{\xi}_k(t)$ is a slowly fluctuating mean field (which is a vector field) defined by the average

$$\xi_k^\alpha(t) = \left\langle \sum_{k'} V_{kk'}^{\alpha\beta} \sigma_{k'}^\beta \right\rangle \qquad (351)$$

To see what $\xi_k(t)$ looks like, let us suppose what is usually the case, viz., that T_1 is much longer than T_2. Then the sort of typical path we will see for $\xi(t)$ is shown below. The occasional T_1 transitions cause a jump of the system between 2 different polarisation groups. On a much shorter timescale, the bath fluctuates between the large number of different states in each polarisation group. The T_2 processes occurring inside a given polarisation group are just restricted random walk processes, and we can take over the well-known theory of random walks to deal with them.



AT LEFT WE SEE THE DENSITY OF BATH STATES. AT RIGHT A PLOT OF THE BATH ENERGY IN TIME, SHOWING BOTH THE RAPID T_2 FLUCTUATIONS INSIDE A POLARISATION GROUP, AND OCCASIONAL T_1 "JUMPS" BETWEEN THEM.

We should emphasize that in this discussion we are only considering the effect of the bath fluctuations driven by the $V_{kk'}$; under these circumstances we expect T_1 to be very long, depending on the form of $V_{kk'}$ (recall that a dipolar form for $V_{kk'}$ will drive T_1 transitions since dipolar interactions do not conserve spin - but such dipolar interactions are typically very weak).

On the other hand the moment we couple the qubit to the spin bath, the diagonal processes discussed above will drastically increase the rate at which spins in the bath flip between different polarisation groups. Thus if we were able to actually measure T_1 in the bath, we would find that T_1 drops suddenly once the qubit dynamics switches on.

Let us formulate therefore the intrinsic bath dynamics assuming that $T_1 \to \infty$. We have a noise field $\xi(t)$ acting on bath spin, and what we would like to do is evaluate the correlator

$$K(t_1-t_2) = \langle \tilde{\epsilon}(t_1)\, \tilde{\epsilon}(t_2) \rangle \qquad (352)$$

where $\tilde{\epsilon}(t)$ is the total bias. In the standard theory of noise processes this correlator specifies a Probability $\mathcal{P}[\tilde{\epsilon}(t)]$ for a "noise path" $\tilde{\epsilon}(t)$, given by

$$\mathcal{P}[\tilde{\epsilon}(t)] = e^{-\frac{1}{2}\int dt_1 \int dt_2\, \tilde{\epsilon}(t_1) K^{-1}(t_1-t_2)\, \tilde{\epsilon}(t_2)} \qquad (353)$$

assuming that we have Gaussian correlated noise (ie., that higher order correlations between $\tilde{\epsilon}(t)$ are all just cumulants involving $K(t_1-t_2)$). If the noise is of random walk form then it is "diffusive" in time, ie., we must have

$$\langle (\tilde{\epsilon}(t_1) - \tilde{\epsilon}(t_2))^2 \rangle = \Lambda^3 |t_1-t_2| \qquad (354)$$

where Λ is a constant; to be consistent with (352), this means we require

$$\left.\begin{aligned} K(t_1-t_2) &= \tfrac{1}{2}\left(\langle \tilde{\epsilon}^2(t_1)\rangle + \langle \tilde{\epsilon}^2(t_2)\rangle - \langle (\tilde{\epsilon}(t_1) - \tilde{\epsilon}(t_2))^2 \rangle \right) \\ &= \tfrac{1}{2}\Lambda^3 \left(|t_1| + |t_2| - |t_1-t_2| \right) + \tilde{\epsilon}(t=0) \end{aligned}\right\} \qquad (355)$$

The constant Λ is related to T_2 as follows. Since the flip rate for each spin is T_2^{-1}, and since moreover the strength of the interaction $V_{kk'}$ between 2 spins engaging in a T_2-process is also $|V_{kk'}| \sim T_2^{-1}$, we have

$$\Lambda^3 \sim \Gamma_M T_2^{-1} \qquad (356)$$

for a bath in the M-th polarisation group.

The effect of these noise processes on the dynamics can be handled in various ways, depending on taste. One way is to calculate the effect on the influence functional directly, going back to eq. (213). We will not go through this exercise here, but instead just make quick heuristic remarks.

Consider the amplitude $A_{\Uparrow\Uparrow}(t)$ for the qubit to remain in the state $|\Uparrow\rangle$ during a time t, under the influence of the noise. We can expand this in powers of Δ_0, as follows:

$$A_{\Uparrow\Uparrow}(t) = 1 - \Delta_0^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \left\langle e^{i\int_{t_2}^{t_1} d\tau\, \tilde{\epsilon}(\tau)} \right\rangle + O(\Delta_0^4) \qquad (357)$$

where the average $\langle \cdots \rangle$ is weighted by the Gaussian functional in (353). Now (357) is easily computed - it is just a special case of the characteristic functional for a Gaussian process, so that

$$\left\langle e^{i\int_{t_2}^{t_1} d\tau\, \tilde{\epsilon}(\tau)} \right\rangle = e^{-\frac{1}{6}\Lambda^3(t_1-t_2)^3 + \frac{i}{2}\tilde{\epsilon}_0(t_1-t_2)} \qquad (358)$$

so that

$$A_{\Uparrow\Uparrow}(t) = 1 - \Delta_0^2 \int_0^t dt_1 \int_0^{t_1} dt_2\, e^{-\frac{1}{6}\Lambda^3(t_1-t_2)^3 + \frac{i}{2}\tilde{\epsilon}_0(t_1-t_2)} + \cdots \qquad (359)$$

From this we can see what the structure of the whole series is - the 2nd-order term is easily evaluated by dropping the term in $\tilde{\epsilon}_0$ (this initial bias is averaged over later on) to get

$$\left.\begin{aligned} A_{\Uparrow\Uparrow}(t) &= 1 - \Delta_0^2 t \int du\, e^{-\frac{1}{6}\Lambda^3 u^3} + \cdots \\ &\sim 1 - \Delta_0^2 t/\Lambda + \cdots \end{aligned}\right\} \qquad (360)$$

Summing this series is clearly going to give an exponential decay at a rate $\Gamma \sim O\left(\Delta_0^2/\Lambda\right)$ in this limit

(ii) Summary of General Averaging Results : Let us now summarize what all these path integral manipulations have led to. We do this for the central spin model, without attempting a more general exposition.

The remarkable thing is that we can reduce the problem of integrating out the bath spins to one of simple integrals, as opposed to functional integrals. This is much simpler therefore than the analogous spin-boson problem. These integrals are so simple basically because we are dealing with the dynamics of bath spins, which move in a much simpler Hilbert space than oscillators. Thus we can not only reduce the functional integrals down to ordinary integrals, but also go beyond weak-coupling.

The averages are as follows:

(i) Precessional Phase Average: given by $$\int_0^\infty dy\, e^{-y} \qquad (361)$$

(ii) Topological Phase Average: given by $$\sum_{\nu=-\infty}^{\infty} F_\lambda(\nu) \int_0^{2\pi} \frac{d\varphi}{2\pi}\, e^{-2i\nu\varphi} \qquad (362)$$

(iii) Energy Bias Average: given by
$$\left.\begin{aligned} &\int d\epsilon\, G_M(\epsilon)\, \frac{e^{-\beta\epsilon}}{Z_M(\beta)} \quad (M \text{ fixed}) \\ &\int d\epsilon\, W(\epsilon) \sum_M \frac{e^{-\beta\epsilon}}{Z(\beta)} \quad (\text{sum over } M) \end{aligned}\right\} \qquad (363)$$

(iv) Bath Fluctuation Average: given by $$\int \mathcal{D}\tilde{\epsilon}(t)\, e^{-\frac{1}{2}\int dt \int dt'\, \tilde{\epsilon}(t) K^{-1}(t-t') \tilde{\epsilon}(t')} \qquad (364)$$

We have seen all these averages in the above, except that we have not previously written out the energy bias averages. The energy bias averages assume a spin bath in thermal equilibrium, but one can imagine a situation in which the timescale $t \ll T_1$, so that there are no intrinsic bath fluctuations between different M, and when the precessional bath dynamics cycles the bath between M and $-M$; in this case, there is no need to sum over M, if we are dealing with a single central spin.

Note that these averages are specific to a central system in which one can distinguish between diagonal and non-diagonal terms in $\mathcal{H}_{eff}$. It is this that leads to the distinction between Precessional & Topological phase averages. In a more general situation we would not make this distinction.

The obvious question is - what do we average over? The answer is, we average over the free central system dynamics, with parameters "renormalized" by the addition of phases & biases.

In the case of the central spin problem, we apply the averages to the "bare" function $\rho^{(0)}_{\sigma\sigma'}(t;\varphi,y,\epsilon)$ which contains the renormalized tunneling splitting

$$\Delta_M(\varphi,y) = \Delta_0 \left|\cos\varphi\, J_M(2\sqrt{\kappa y})\right| \qquad (365)$$

where κ is given by (346). We then apply the averages in turn to get a final result for the full reduced density matrix $\bar{\rho}_{\sigma\sigma'}(t)$.

As an example we consider again the evaluation of $\bar{\rho}_{\Uparrow\Uparrow}(t)$, in an external bias field ϵ_0. We first calculate

$$\mathcal{P}^M_{\Uparrow\Uparrow}(t,\epsilon) = \int_0^\infty dy\, e^{-y} \sum_{\nu=-\infty}^{\infty} F_\lambda(\nu) \int_0^{2\pi} \frac{d\varphi}{2\pi}\, e^{-2i\nu\varphi} \left[1 - \frac{\Delta_M^2(\varphi,y,\epsilon)}{E_M^2(\varphi,y,\epsilon)} \sin^2 E_M(\varphi,y,\epsilon)\right] \qquad (366)$$

which takes account of the precessional & topological phase averages. We then do a bias average, by averaging over all the spin bath states with the appropriate weight:

$$P_{\uparrow\uparrow}(t,\epsilon_0) = \int d\epsilon \sum_{M=-N}^{N} \frac{e^{-\beta\epsilon}}{Z(\beta)} G_M(\epsilon) \; P_{\uparrow\uparrow}^{M}(t,\epsilon+\epsilon_0) \qquad (367)$$

In these eqtns we assume that the bath is in thermal eqtbm, and that we have no specification of M (we sum over a thermal ensemble); and we define

$$E_M^2(\varphi,y;\epsilon) = \epsilon^2 + \Delta_M^2(\varphi,y) \qquad (368)$$

As discussed previously, typically we can assume a form

$$\left.\begin{aligned} G_M(\epsilon) &= C_M^{\frac{1}{2}(N+M)} \, \bar{g}_M(\epsilon) \\ g_M(\epsilon) &\sim \left(\frac{2}{\pi\Gamma_M^2}\right)^{1/2} e^{-2/\Gamma_M^2(\epsilon+M\omega_0)^2} \end{aligned}\right\} \qquad (369)$$

for the density of states. Finally, if we need to deal with slow fluctuations of the bath bias, then we need to include the fluctuational average. This is most important over longer times - in this case we should write

$$\left.\begin{aligned} \rho_{\uparrow\uparrow}^{(0)}(t;\varphi,y,\epsilon) &= e^{-t/\tau_M(\varphi,y)} \qquad [\text{relaxation}]. \\ \text{instead of} \qquad & \\ \rho^{(0)}(t,\varphi,y,\epsilon) &= 1 - \frac{\Delta_M^2(\varphi,y)}{E_M^2(\varphi,y,\epsilon)} \sin^2(E_M(\varphi,y,\epsilon)\,t) \quad [\text{coherent}] \end{aligned}\right\} \qquad (370)$$

and then average over this relaxational form to get

$$P_{\uparrow\uparrow}(t) = \int d\epsilon \sum_{M=-\infty}^{\infty} \frac{e^{-\beta\epsilon}}{Z(\beta)} G_M(\epsilon) \int dy\, e^{-y} \sum_{\nu=-\infty}^{\infty} F_\lambda(\nu)\, e^{-2i\nu\varphi}\; e^{-t/\tau_M(\varphi,y)} \qquad (371)$$

where the relaxation time is

$$\left.\begin{aligned} \tau_M(\varphi,y) &= \Delta_M^2(x,\varphi) \int d\epsilon\, G_M(\epsilon) \int ds\, e^{i\epsilon s}\, e^{-\frac{1}{6}\Lambda^3 s^3} \\ &\xrightarrow[\Gamma_M T_2 \gg 1]{} \Delta_M^2(x,\varphi) \big/ \pi^{1/2}\,\Gamma_M \end{aligned}\right\} \qquad (372)$$

We emphasize here that all of the averages over ϵ and M are assuming a thermal bath state. One can also imagine a situation in which the bath is "prepared" in some more specific state. We do not discuss this case here.

(b) Some Results for Central Spin Dynamics

As in the case of the spin-boson system, these results are of considerable importance for experiments on a wide variety of physical systems. Let us briefly here examine some special cases, which are not only of academic interest, but also can be applied to real systems. We shall consider here 2 particular cases, and then make some remarks about when and how a central spin system can be reduced to a spin-boson model. Many other limiting cases have been discussed in the literature.

(i) Strong Precessional Decoherence

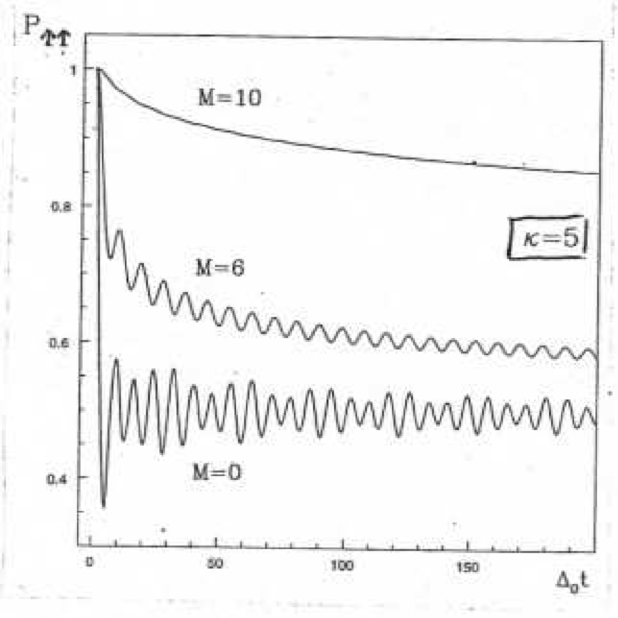
: Let us begin by considering the case where the dynamics is dominated by the precession of the bath spins in between the tunneling flips of the qubit, ie., where we have

$$\left.\begin{array}{lll} \kappa \gg 1, & \text{where} & e^{-\kappa} = \prod_k |\cos\beta_k| \\ & & \\ \text{with} & \beta_k = & \left.\begin{array}{ll} |\omega_k / h_k| & (\omega_k \ll h_k) \\ |h_k/\omega_k| & (\omega_k \gg h_k) \end{array}\right\} \end{array}\right\} \quad (373)$$

and we note that from (373) we have

$$\kappa \sim \left\{\begin{array}{ll} \frac{1}{2}\sum_k |\omega_k/h_k|^2 & \omega_k \ll h_k \\ \frac{1}{2}\sum_k |h_k/\omega_k|^2 & \omega_k \gg h_k \end{array}\right\} \quad (374)$$

Let us assume here that all the polarisation groups merge together, and so $W(\epsilon)$ is a simple Gaussian - and let us also assume for simplicity that kT is large compared to ω_0, the typical coupling to the bath spins. Then we have the following general picture.



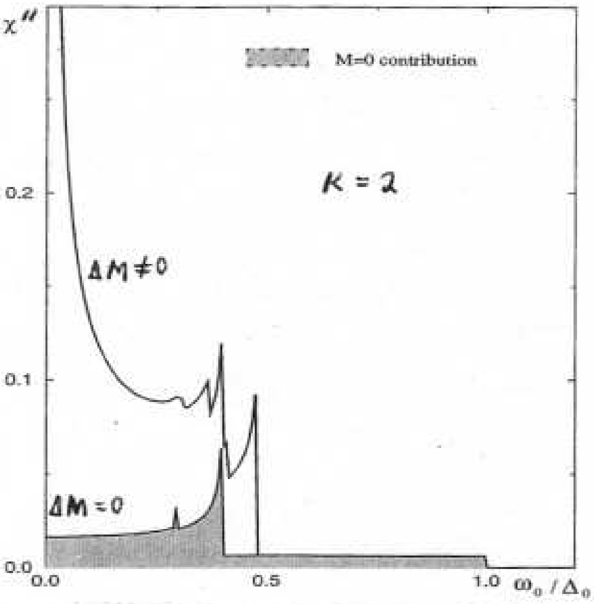
We first note that the function $P_{pp}^M(t,\epsilon)$ for the different polarisation groups decay in quite different ways. The reason is connected with the discussion given between eqtns (317) and (318); when we deal with the M-th polarisation group, a minimum of M bath spins is "flipping" in the course of the time evolution of the systems between qubit flips, and this causes strong decoherence if $M \gg 1$.

If we now add all the P_M together, the net result looks very roughly like a log t relaxation, although we do not give the forms here. We notice that this relaxation in $P_{11}(t)$ is purely a result of decoherence - it does not in any way involve dissipation.

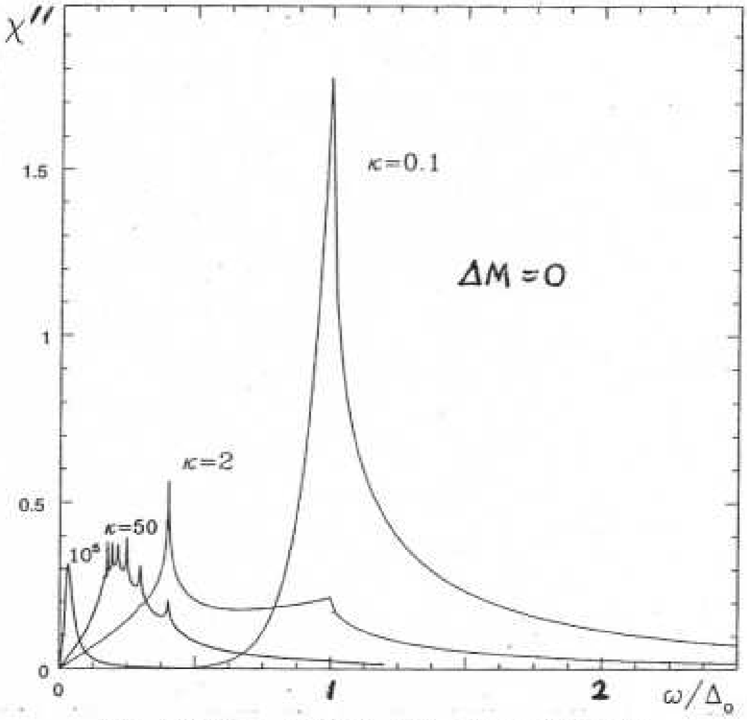
The structure of the relaxation in t-space seems at first to be quite boring. However if we Fourier transform to the frequency domain we find that it actually quite peculiar. Let us define

$$\chi(\omega) = \int dt\, P_{\Uparrow\Uparrow}(t)\, e^{i\omega t} \qquad (375)$$

so that $\mathrm{Im}\,\chi_{\Uparrow\Uparrow}(\omega)$ tells us the "absorptive" part of the dynamics. In the figures below we see that there is a set of peaks in $\chi''_{\Uparrow\Uparrow}(\omega) \equiv \mathrm{Im}\,\chi_{\Uparrow\Uparrow}(\omega)$, with the



THE FUNCTION $\chi''(\omega)$ FOR A CENTRAL SPIN WHEN $\kappa = 2$, SHOWING THE "COHERENT" ($\Delta M = 0$) AND INCOHERENT CONTRIBUTIONS



THE FUNCTION $\chi''(\omega)$ FOR THE COHERENT ($\Delta M = 0$) CONTRIBUTIONS ONLY, FOR VALUES OF κ RANGING FROM 0.1 TO 10^5.

number of these peaks varying with κ (in fact there are $\sim O(\kappa)$ different peaks). Of particular interest is the spectrum for $M = 0$; One finds

$$P^{M=0}_{\Uparrow\Uparrow}(t) = 1 - \int_0^\infty dy\, e^{-y}\, 4A(y) \sum_{l=0}^{\infty} J_{2l+1}(\Delta_0(y) t) \qquad (376)$$

so that

$$\mathrm{Im}\,\chi^{M=0}_{\Uparrow\Uparrow}(\omega) = \frac{2}{\omega} \int dy\, e^{-y} A(y) \frac{|\Delta_0(y)|}{(\omega^2 - \Delta_0^2(y))^{1/2}}\, \theta(\omega - |\Delta_0(y)|) \qquad (377)$$

where A is a constant dependent on the initial condition, and $A(y) = A\,|J_0(2\sqrt{\kappa y})|$. Thus we see that even the $M=0$ sector is not a completely coherent δ-function in frequency space - this is because even if $M = 0$, we still have both spin flips.

(ii) <u>Strong Topological Decoherence</u>: The simplest example of topological decoherence arises if we take the toy model described by the Hamiltonian

$$\mathcal{H}_{Top} = \Delta_0 \tau_x \cos\Big(\sum_k \underline{\alpha}_k \cdot \underline{\sigma}_k\Big) \qquad (378)$$

which was introduced in (328). (as well as the generalisation where the phase in the cosine is $(\underline{\Phi}_0 + \sum_k \underline{\alpha}_k \cdot \sigma_k))$. Let's consider the simple example where $\epsilon_0 = 0$, and so the system dynamics are given by

$$\bar{\rho}_{\sigma\sigma'}(t) = \sum_{\nu=-\infty}^{\infty} \int_0^{2\pi} \frac{d\varphi}{2\pi} e^{-i\nu\varphi} F_\nu \rho^{(0)}_{\sigma\sigma'}(t, \Delta_0(\varphi)) \qquad \begin{pmatrix} \epsilon_0 = 0 \\ \text{Topological limit} \end{pmatrix} \tag{379}$$

where
$$\rho^{(0)}_{\sigma\sigma'}(t, \Delta_0(\varphi)) = \begin{pmatrix} \cos^2(\Delta_0(\varphi)t) & i\sin(\Delta_0(\varphi)t)\cos(\Delta_0(\varphi)t) \\ -i\sin(\Delta_0(\varphi)t)\cos(\Delta_0(\varphi)t) & \cos^2(\Delta_0(\varphi)t) \end{pmatrix} \tag{380}$$

is the free qubit propagator including the phase φ. Now consider the factor F_ν, which is given by

$$F_\nu = \prod_{k=1}^{N} \cos(2\nu\alpha_k) \xrightarrow[|\alpha_k| \ll 1]{} e^{-4\lambda\nu^2} \tag{381}$$

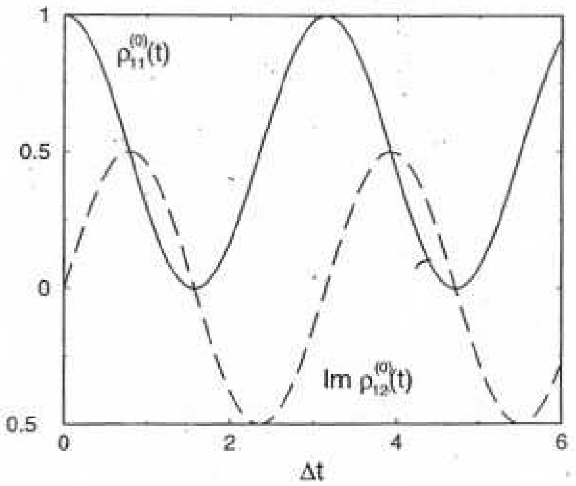
where
$$\lambda = \frac{1}{2} \sum_k |\underline{\alpha}_k|^2 \tag{382}$$

Now we notice that when $\lambda > 1$, $F_\nu \sim \delta_{\nu 0}$ + small corrections

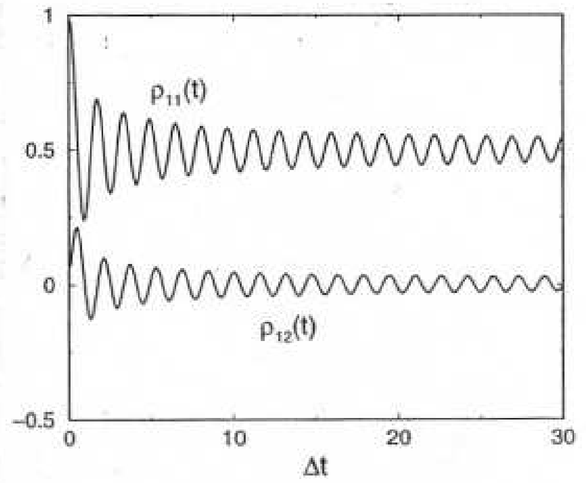
so that
$$\left.\begin{aligned} &F_\nu \sim \delta_{\nu 0} + \text{small corrections} \\ &\bar{\rho}_{\sigma\sigma}(t) = \int_0^{2\pi} \frac{d\varphi}{2\pi} \rho^{(0)}_{\sigma\sigma'}(t, \Delta_0(\varphi)) \end{aligned}\right\} \tag{383}$$

Thus, e.g., we find that
$$\bar{\rho}_{\uparrow\uparrow}(t) = \frac{1}{2}[1 + J_0(2\Delta_0 t)] \tag{384}$$

and the general effect of the topological decoherence is a suppression of the oscillations. We see this in the comparison below, in the figures.



. Diagonal and off-diagonal of the density matrix for a "Free spin", uncoupled from the environment, and in zero bias field ($\xi = 0$).



. Diagonal and off-diagonal elements of the density matrix in the central spin problem with zero bias, and with topological decoherence dominating. The value of the topological decoherence parameter is relatively weak: $\lambda = 1/8$.

This topological decoherence persists in the analysis of the full problem, with averaging over precessional decoherence and energy. We do not quote the results here as they are rather lengthy. There are many interesting different limiting cases of the central spin model, which are analysed in the literature. The result depend in general on the bias ϵ_0, the temperature T, the strengths of precessional and topological decoherence (measured by K and λ), and the bath fluctuational dynamics.

(iii) Weak-Coupling Limit - Reduction to Spin-Boson Model: An interesting question that arises is under what circumstances the central spin model reduces to the spin-boson model. This is a special case of a more general question, which is under what circumstances a spin bath can be reduced to an oscillator bath.

From the general Born-Oppenheimer arguments that we gave for the reduction to an oscillator bath, it is clear that these derivations fail for a spin bath not only because the couplings are not small (recall that Born-Oppenheimer can deal with strong coupling) but also because there is no sharp separation of timescales of the kind we need for Born-Oppenheimer to work. A thorough investigation of this point is lengthy, because we have to look at all the various possible transitions in the spin bath that can be excited by the coupling to the central system; but it should be fairly obvious already that the existence of dissipation-free (or almost dissipation-free) processes which cause strong decoherence, is a signal that there is a problem. This shows clearly that there are important couplings to the bath in which little or no energy exchange is involved, so that the Born-Oppenheimer criterion (223) is failing.

There are however cases where one can map to an oscillator bath. This is seen physically in the weak coupling limit, i.e., where

$$\left.\begin{aligned} |\omega_k| &\ll \Delta_0 \\ |h_k| &\ll \Delta_0 \end{aligned}\right\} \qquad (385)$$

in the central spin model. In this case the effect of the bath is negligible unless either λ or κ is appreciable, which requires a very large number N of spin bath modes - we need

$$N \gtrsim (\Omega_0/\omega_k)^2 \qquad (386)$$

to get $\lambda \gtrsim O(1)$. Note however that in practical applications with qubits, we may well require a large value for Δ_0. In this case the mapping to an oscillator bath is of some interest. Consider, e.g., the system described by

$$\mathcal{H}_{eff} = \Delta_0 \hat{\tau}_x + \sum_k (\underline{h}_k \cdot \sigma_k + \tau_z \underline{\omega}_k \cdot \underline{\sigma}_k) \qquad (387)$$

which we already studied, but now let

$$\left.\begin{aligned} h_k, \omega_k &\ll \Delta_0 \\ |\omega_k / h_k| &\ll 1 \end{aligned}\right\} \qquad (388)$$

Now we can expand the path dynamics we previously studied (eqtns. (323)-(327)) in a perturbative expansion, to 2nd order in $\underline{\omega}_k$; in this way we get back an influence functional of oscillator form.

Another case where a mapping to an oscillator bath is possible is if $V_{kk'}$ is not small. If $|V_{kk'}| > |h_k|, |\omega_k|$, then the bath spins couple together to form spin wave excitations, which then can be represented as oscillators.

REFERENCES to PART 2, SECTION A

① PARAMAGNETIC & KONDO SPINS

(a) D. van der Marel, GA Sawatzky, Phys. Rev. B37, 10674 (1988)
" " , Sol. St. Comm. 55, 937 (1985)
D.L. Cox, A Zawadowski, Adv. Phys. 47, 599 (1998)
G. Gruner, Adv. Phys. 23, 941 (1974)
A.C. Hewson, "The Kondo Problem to Heavy Fermions", CUP (1993)
G. Gruner, A Zawadowski, Rep. Prog. Phys. 37, 1497 (1974)
J.R. Schrieffer PA Wolff, Phys. Rev. 149, 491 (1966).

(b) VJ Emery A Luther, Phys. Rev. B9, 215 (1974)
AJ Leggett et al., Rev. Mod. Phys. 59, 1 (1987)

(c) HM Rønnow et al., Science 308, 389 (2005), & refs. therein
J. Jensen, AR Mackintosh, "Rare Earth Magnetism" (Clarendon, 1991)
M. Schechter, PCE Stamp,

(d) GA Fiete, EJ Heller, Rev. Mod Phys 75, 933 (2003)
HC Manoharan, CP Lutz, DM Eigler, Nature 403, 512 (2000)

The first set of papers deals with the Kondo problem, for transition metal ions in the main. The papers of van der Marel & Sawatzky deal with the derivation of parameters in the microscopic models, and the Schrieffer with the transformation to the Kondo model. The remaining papers & books in (a) review the Kondo model & its application.

The papers in (b) discuss the mapping between the Kondo problem & the spin-boson model.

The papers in (c) discuss Rare Earth ions, with particular attention to the $LiHo_xY_{1-x}F_4$ system.

The papers in (d) look at the "Quantum Corral" with Kondo impurities inside the corral.

② MAGNETIC MOLECULES, METALLIC MAGNETIC CLUSTERS

(a) A. Caneschi et al., J. Mag. Mag. Mat 200, 182 (1999)
W. Wernsdorfer, Adv. Chem. Phys. 118, 99 (2001)
B. Barbara et al., J. Mag. Mag. Mat. 200, 167 (1999)
I. Tupitsyn, B. Barbara, in "Magnetism, Molecules to Materials III (ed JS Miller, M Drillon, Wiley, 2001).
W Wernsdorfer, R Sessoli, Science 284, 133 (1999)

(b) R. Giraud et al., Phys. Rev. Lett. 87, 057203 (2001)
" , Phys. Rev. Lett. 91, 257204 (2003)

(c) A. Morello et al., Phys. Rev. Lett., 93, 197202 (2004)
M. Evangelisti et al., Phys. Rev. Lett., 95, 227206 (2005)

(d) JL van Hemmen A Suto, Physica B141, 37 (1986)
M. Enz R Schilling J Phys. C19, 1765 (1986); ibid L711 (1986)
MV Berry, Proc. Roy Soc. A392, 45 (1984)
FDM Haldane, Phys. Rev. Lett. 50, 1153 (1983)
A Shapere, F Wilczek "Geometric Phases in Physics" (World Sci., 1989)
EN Bogachek A Krive, Phys. Rev. B46, 14559 (1992)
A. Garg, Europhys. Lett. 22, 205 (1993)
NV Prokof'ev PCE Stamp, J. Low Temp. Phys. 104, 143 (1996)
PCE Stamp, EM Chudnovsky, B Barbara, Int. J. Mod. Phys. B6, 1355 (1992)

(e) G. Schmid, Polyhedron 7, 2321 (1988)
WP Halperin, Rev Mod Phys. 58, 533 (1986)
A. Simon, Angew Chem Int. Ed. Engl. 27, 159 (1988)
"Physics & Chemistry of Metal Cluster Compounds", ed LJ de Jongh (Kluwer, 1994)

The first set of papers in (a) review the early experimental work on the quantum dynamics of magnetic molecules, except for the last paper of Wernsdorfer & Sessoli, which looks at spin phase effects in quantum tunneling relaxation.

The papers in (b) look at tunneling resonance effects in Ho ions in the $LiHo_xY_{1-x}F_4$ system, with $x \ll 1$; they also see spin-phonon effects.

The papers in (c) look at the rather dramatic effect of molecular spin tunneling on the dynamics of the nuclear spin bath which couples to the tunneling molecular spins.

The papers in (d) are theoretical - the first two give a general discussion of WKB for spin tunneling, and the papers of Berry & Haldane look at the topological spin phase - this whole topic is reviewed by Shapere & Wilczek. The variation of Berry phase in an applied field is discussed by Bogachek & Krive, & Garg. The last 2 papers discuss how spin tunneling dynamics is modified by the coupling to phonons, electrons, & nuclear spins.

The papers in (e) discuss metallic clusters; the paper of Halperin is a review from the mesoscopics standpoint, whereas the book of de Jongh concentrates on experiments & materials science.

③ SPIN-BOSON & CENTRAL SPIN MODELS

(a) S. Coleman "The Whys of Symmetry" (CUP, 1985)
L. Schulman, "Techniques & Applications of Path Integration" (Wiley, 1981) } Instantons

(b) AJ Leggett et al., Rev. Mod Phys. 59, 1 (1987)
AJ Leggett, Phys. Rev B30, 1208 (1984)
AO Caldeira AJ Leggett, Ann Phys 149, 374 (1983)
RP Feynman FL Vernon, Ann Phys. 24, 118 (1963) } Oscillator Baths

(c) NV Prokof'ev PCE Stamp J. Phys. CM 5, L663 (1993)
" " Rep. Prog. Phys. 63, 669 (2000)
PCE Stamp, Studies Hist & Phil. Mod Phys. 37, 467 (2006) } Spin Bath.