Spin-based quantum computers made by chemistry: hows and whys†

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This introductory review discusses the main problems facing the attempt to build quantum information processing systems (like quantum computers) from spin-based qubits. We emphasize 'bottom-up' attempts using methods from chemistry. The essentials of quantum computing are explained, along with a description of the qubits and their interactions in terms of physical spin qubits. The main problem to be overcome in this whole field is decoherence—it must be considered in any design for qubits. We give an overview of how decoherence works, and then describe some of the practical ways to suppress contributions to decoherence from spin bath and oscillator bath environments, and from dipolar interactions. Dipolar interactions create special problems of their own because of their long range. Finally, taking into account the problems raised by decoherence, by dipolar interactions, and by architectural constraints, we discuss various strategies for making chemistry-based spin qubits, using both magnetic molecules and magnetic ions.

I. Introduction

The basic question addressed in this short review is: how might one build a spin-based quantum computer using the 'bottom-up' methods of chemistry? Before even starting on this topic, the reader might suppose that we should first answer two other questions, viz. (i) can one build a quantum computer at all? (ii) why would this be a subject for chemists?

The answer to the first question is not known. Although one can easily imagine various schemes for doing quantum infor-

mation processing, to actually build a 'Quantum Information Processing System' (QIPS) one has to deal with a really quite fundamental problem in Nature, usually called the 'decoherence problem'. Quantum computing involves manipulating 'multiply entangled wave-functions', involving many different sub-systems in the QIPS—in these terribly complex quantum states, distributed over the whole QIPS, the individual wave-functions of the individual components lose all meaning and only the wave-function of the entire system is physically meaningful. The problem is that such states are extremely delicate, and can be destroyed by very weak interactions with their surroundings—and yet in order to use them we need to be able to probe and manipulate them. Physicists and chemists working in 'nano-science' have come up with many designs, and there has been considerable success in building QIPS involving just a few entangled 'qubits' (the simplest kind of sub-system, involving

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only two quantum states). This success has simply made the importance of the decoherence problem more obvious—solving it will be the key that unlocks the QIPS door (and doubtless many other doors as well).

Concerning the second question—so far the most successful designs for QIPS have been made from ion traps,[1] but it is not yet clear how one might scale these up to the larger systems, involving many entangled qubits, that are needed for quantum computation. The most likely designs may be hybrids having 'solid-state' circuits of qubits, with communication effected by photons—nobody really knows yet. There are then 2 good reasons for concentrating on spin-based systems, made using bottom-up methods. The first is that a device which only uses spin degrees of freedom avoids moving charges around—this is good because moving charges invariably causes decoherence. The second is that if the basic sub-units are made by Nature (in the form of molecules or ions) then quantum mechanics guarantees they will all be identical, provided we can eliminate impurities, defects, etc. This of course takes us into the realm of chemistry.

In writing this review we have assumed a reader who may not be too familiar with this subject, but who is interested in understanding the main ideas and problems, and who is also looking for suggestions for future work in this area. We therefore begin, in section II, by describing briefly what a QIPS is, and how one would describe its physical components if they were indeed made from spin qubits using chemistry. This description also includes a discussion of the physical mechanisms responsible for decoherence in such systems. Given the importance of decoherence, we have devoted all of section III to how it works. The emphasis is on simple pictures, which often convey a better feeling for what is going on than complex mathematics. Then, in section IV, we outline some features of the chemistry, and a few desiderata for any future architecture. This allows us to make some suggestions for future work. This last section is necessarily open-ended—at present nobody knows which designs may ultimately succeed.

II.   Describing the system

Physicists and chemists on the one hand, and computer scientists on the other, have quite different ways of describing a system whose ultimate aim is to do computing (quantum or classical). Each kind of description is valuable, but the differences often cause misunderstanding. In this section we describe and then connect the two kinds of description; we then discuss an effective Hamiltonian for a set of qubits made from real materials.

A.   Description in computational language

Computer scientists like to reduce physical computational systems to "Turing machines";[2] a clear physical discussion of this was given by Feynman.[3,4] In a Turing machine, a "tape" moves forward or backwards past a "head"; the head has the job of writing in or reading out particular discrete states (labelled by different symbols) on the tape (and it may also erase states). There is also a table of instructions which tell the tape and head what to do (the "program"), and a "stable register" or memory, which stores the state of the machine at any given time. (Turing
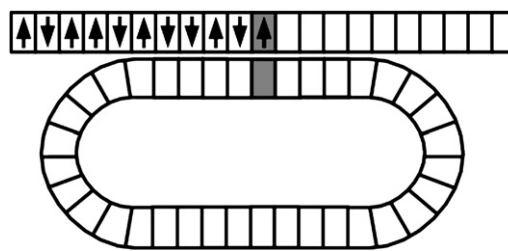

Fig. 1 Cartoon view of a Turing machine: a head (shown shaded) on a control loop reads and writes onto a linear "tape". The states of both are binary (shown here as spins). We do not show the register or the program parts of the machine.

thought of this as being analogous to the state of mind of a sentient being.) The net result is shown in Fig. 1. Note that the state of a Turing machine at any time can be understood in binary code as a string of 1s and 0s (or a sequence of on/off states, or up/down, or heads/tails, etc.).

Even though real computers may not be constructed like a Turing machine (indeed Turing machines provide a very clumsy model for a realistic computing architecture), nevertheless any computer can be mapped, in its logical and operational structure, to a Turing machine. Moreover, Turing showed that a rather simply constructed machine of this kind (since made even simpler) could do any discrete computation. Thus all digital computers can be described in terms of such "universal (classical) Turing machines".

This idea of classical Turing machines can be enlarged to cover quantum Turing machines, in which the notion of a state is generalised to include the usual quantum superpositions of states, in the head, tape, register and program.[4-6] This generalisation seems straightforward—however the way one describes such a system has led to much misunderstanding and a severe divergence in the literature. Computer scientists like to talk in terms of states, and logical operations on them—in quantum computing these operations are called "unitaries". A "*quantum computation*" is then a sequence of unitary transformations $\hat{U}_N = \prod_k \hat{u}_k$ performed on some initial state $|\Psi_f\rangle$, to produce the final state $|\Psi_f\rangle$. The initial state is then the input to the computer, and the final state the output.

These states are a quantum mechanical generalisation of the binary strings mentioned above—however they are much more complicated. Consider, *e.g.*, a classical pair of binaries, which can be in one of four states (i.e., (11), (10), (01), or (00)). In quantum mechanics, systems that have 2 states are called 'two-level systems' (TLS), or 'qubits'. Now however a single qubit can exist in an arbitrary superposition of states $|\Psi_1\rangle = a_0 e^{i\phi_0}|0\rangle + a_1 e^{i\phi_1}|1\rangle$, where the coefficients a_0, a_1 are real, $a_0^2 + a_1^2 = 1$, the states $|0\rangle$ and $|1\rangle$ correspond to the original classical states (0) and (1), and ϕ_0, ϕ_1 are phases. A *pair* of qubits has the general wave-function

$$|\Psi_2\rangle = a_{00}e^{i\phi_{00}}|00\rangle + a_{10}e^{i\phi_{10}}|10\rangle + a_{01}e^{i\phi_{01}}|01\rangle + a_{11}e^{i\phi_{11}}|11\rangle \quad (1)$$

and we see that if we have N qubits then we will end up with 2^N coefficients and 2^N 'relative phases' (of which one is redundant). The great power of quantum computation resides in all the information that can be stored in these phases, allowing one to 'superpose' many computations at once.[6] A key feature of these

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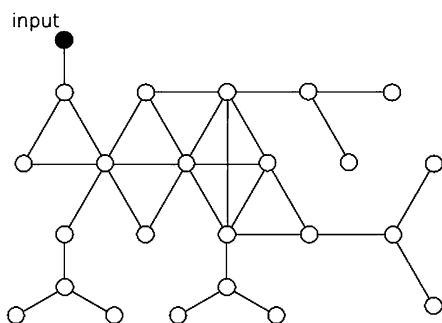*J. Mater. Chem.*, 2009, **19**, 1718–1730 | 1719

Fig. 2 In a quantum walk, the system "hops" between nodes, each of which represents a state in the Hilbert space of the QIPS. Allowed transitions are shown as links between the nodes.

states is that typically the N qubits are '*entangled*'; one cannot write them as a product over independent wave-functions for each individual qubit. As first noted by Einstein,[7] this leads to very counter-intuitive features—it is simply not correct to assign a quantum state to an individual qubit, and only the N-qubit wave-function, existing with all its relative phases in a vast 2^N-dimensional Hilbert space, is physically meaningful.

The above description is very abstract. To get a more intuitive understanding, it is helpful to map the QIPS onto a "quantum walk" system, in which a single particle hops around a graph (Fig. 2). Each node of the graph represents a state in the Hilbert space of the QIPS, and the links between the nodes represent the transition matrix elements (in general time-dependent) between them. Thus the time evolution of a QIPS can be represented as a "quantum walk" in information space;[8] and it is always possible to make this mapping for a QIPS composed of qubits.

To see how this works one needs to specify a Hamiltonian, to give the system dynamics. The simplest quantum walk Hamiltonians take the form:[9]

$$\hat{H}_{QW} = \sum_{\mu\nu}\left[T_{\mu\nu}(t)c_\mu^\dagger c_\nu + H.c.\right] + \sum_\mu \varepsilon_\mu(t)c_\mu^\dagger c_\mu \qquad (2)$$

where the operators $c_\mu^\dagger$, c_μ create or destroy a particle at the μ-th node, $\varepsilon_\mu(t)$ is the μ-th node energy, and $T_{\mu\nu}(t)$ the non-diagonal hopping matrix element between nodes μ and ν. This Hamiltonian must be generalized to describe "composite quantum walks" (where discrete internal "spin" variables at each node can also couple to the walker) if we are to fully describe a QIPS.[9] The great advantage of this representation, at least for physicists and chemists, is that we have a good intuitive understanding of how particles move around such graphs. One also clearly sees where things can get complicated, if the ε_μ and $T_{\mu\nu}$ are strongly disordered or if their time-dependence is non-trivial. How this works in practice can be found in the literature.[8,9]

B. Physical description of a QIPS

We now turn to a description of a QIPS of the kind favoured by physicists and chemists, one which will allow them to design and make one, written in terms of the actual physical components of the system. So let us now start from a much more physical model, using a Hamiltonian written in terms of the qubits themselves:

$$\hat{H}_{QB} = \sum_j \vec{B}_j(t)\cdot\hat{\tau}_j + \sum_{ij} U_{ij}^{\alpha\beta}(t)\hat{\tau}_i^\alpha\hat{\tau}_j^\beta \qquad (3)$$

Here the Pauli operator $\hat{\tau}_j$ operates on the j-th qubit, and both the local fields $\vec{B}_j(t)$ and the interaction $U_{ij}^{\alpha\beta}(t)$ can be time-dependent.

Now qubits are real physical objects, and many different physical systems have been proposed to make them. Solid-state examples which have achieved some experimental success include spins in semiconductors and quantum dots,[10] various designs based on superconductors,[11] vacancy centers in diamond,[12] single molecule magnets (SMMs),[13] and rare earth spins.[14] To focus the discussion here, let us consider an example.

An SMM Example: A "Single Molecule Magnet" (SMM) typically has a magnetic core of transition metal (TM) ions, surrounded by a protective cage of organic ligands; the inter-ion couplings are usually antiferromagnetic. A useful (because well-understood) example is the "Fe$_8$" molecule,[15] shown in Fig. 3, in which a core of eight Fe^{3+}, spin-5/2 ions forms a total spin-10 system.

The simplest (and very commonly employed) model of a system like Fe$_8$ starts by reducing the spin Hamiltonian

$$\hat{H}_{SS} = \sum_{ij} J_{ij}^{\alpha\beta}\hat{s}_i^\alpha\hat{s}_j^\beta + \sum_j k_j^{\alpha\beta}\hat{s}_j^\alpha\hat{s}_j^\beta \qquad (4)$$

written in terms of the individual TM spins (for simplicity we ignore here terms like Dzyaloshinski–Moriya interactions) to a single "giant spin" model of form

$$\hat{H}_{GS} = K_2^{\alpha\beta}\hat{S}_\alpha\hat{S}_\beta + K_4^{\alpha\beta\gamma\delta}\hat{S}_\alpha\hat{S}_\beta\hat{S}_\gamma\hat{S}_\delta + \dots \qquad (5)$$

where we assume all low-energy states have the same total spin $\vec{S} = \sum_j \vec{s}_j$. It is very common in the literature to drop many of the higher terms in this—for example, in the case of Fe$_8$ one usually writes the simple biaxial form

$$\mathcal{H}(\mathbf{S}) = -DS_z^2 + ES_x^2 + K_4^\perp\left(S_+^4 + S_-^4\right) - \gamma\mathbf{S}\cdot\mathbf{H}_\perp \qquad (6)$$

which gives a '2-well' crystal field potential acting on $\vec{S}$. Here $D/k_B = 0.23$ K, $E/k_B = 0.094$ K, $K_4^\perp/k_B = -3.28 \times 10^{-5}$ K,
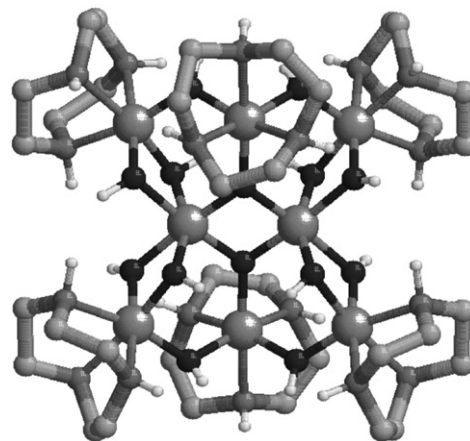

Fig. 3 Simplified ball-and-stick representation of $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ single molecule magnet, showing the octahedral iron ions, the oxo and hydroxo bridges and the 1,4,7-triazacyclononane (tacn) ligands completing the coordination spheres.

$\gamma = g_e \mu_B \mu_0$, and $g_e \approx 2$ is the isotropic g-factor of the spin-10 moment. All the higher terms $\sim O(S^6)$ in eqn (5) are thus dropped. This effective Hamiltonian for Fe_8 is used below roughly 5–10K; above this one certainly has to worry about other states, contained in the more general 10-spin Hamiltonian eqn (4).

At still lower energies one can truncate eqn (5) to its lowest singlet or doublet—in the latter case we have a qubit Hamiltonian of form

$$\hat{H}_{QB}^0 = \vec{B}(\vec{H}_0) \cdot \vec{\tau} \qquad (7)$$

where the effective field $\vec{B}(\vec{H}_0)$ depends both in the crystal field potential and the applied field $\vec{H}_0$. A very important special case of this arises for the 2-well potential, where there is a 'natural basis' for the states, in which $|\uparrow\rangle$ represents the state localised in one well and $|\downarrow\rangle$ the state localised in the other. One then often writes

$$\hat{H}_{QB}^0 \rightarrow \Delta_0\left(\vec{H}_0^\perp\right)\hat{\tau}_x + \varepsilon_0\left(\vec{H}_0^\parallel\right)\hat{\tau}_z \qquad (8)$$

so that $B_x(\vec{H}_0) = \Delta_0(\vec{H}_0^\perp)$; here $\vec{H}_0^\perp$, $\vec{H}_0^\parallel$ are the applied fields perpendicular and parallel to the Fe_8 easy axis. We can think of Δ_0 as an "effective transverse field", driving transitions between the $|\uparrow\rangle$ and $|\downarrow\rangle$ states of the qubit. This effective field can be varied by applying the real external transverse field $\vec{H}_0^\perp$—how it does this is shown for Fe_8 in Fig. 4. The 2-well system possesses a real advantage - it is protected against external transverse field fluctuations, which have a small effect on Δ_o.

Connection between quantum walk and qubit formulations. We have seen that a quantum computer can be thought of as a particle 'walking' in information space, described by a Hamiltonian like eqn (2), or as a set of interaction qubits with Hamiltonian eqn (3). So how do we connect these two? The answer is shown in Fig. 5 for a set of 3 interacting qubits—in
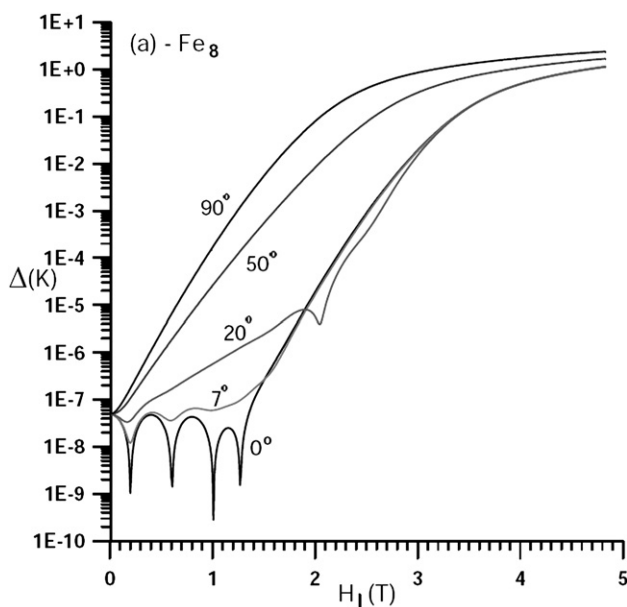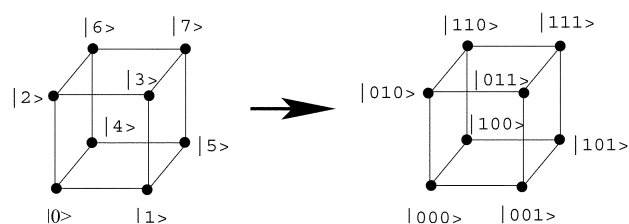

Fig. 5 The states of a 3-qubit system, with 8 states, shown at left in quantum walk representation, and at right in the qubit representation.

general the 2^N states of an N-qubit system map to the corners sites of an N-dimensional hypercube, and the quantum walker hops from one site to another on this hypercube.

How it hops depends on the exact details of the qubit Hamiltonian. Although it is too lengthy to give here, the explicit mapping between the quantum walk Hamiltonian $\hat{H}_{QB}$ in eqn (3) and the qubit Hamiltonian $\hat{H}_{QW}$ in eqn (2), for general qubit couplings, is fairly straightforward—it was given in ref. 9. Another commonly used representation is in terms of "quantum gates",[6] which can also be mapped to quantum walks,[9] and thus also allows a connection to the quantum Turing machine language.

We have seen above how to describe a QIPS in terms of interacting qubits, of a quantum walker, and of a quantum Turing machine (and there are other descriptions—for example, we have for reasons of space ignored adiabatic quantum computation entirely). But how well do such toy models match the real world in which physicists and chemists work? We now address this question.

C. Realistic models of QIPS

Obviously both the general models (2), (3), as well as the specific models (4), (5), and (8) for magnetic molecules, are oversimplified. Many papers have appeared discussing both the failures of general models like (2), (3), or of the simple qubit forms (7) and (8), as well as more specific corrections to the giant spin model (5). Let us begin by enumerating some of the problems of such models as applied to SMMs, and then discuss the more general case. The principal shortcomings are as follows:

1. The giant spin model does not include many other discrete electronic degrees of freedom (spin and charge); if these lie at low enough energies, they couple to $\vec{\tau}$ (and of course to $\vec{S}$). Because they are discrete, they behave like "loose spins" coupling to $\vec{\tau}$ (see refs. 16,17). This happens, for example, if one has structural transformations in the SMM (e.g. Jahn–Teller distortions), or if some exchange couplings J_{ij} are much weaker than others. Note that in a multi-SMM system, there will also be impurities, and "rogue molecules" which are different from the usual SMM because of some internal distortion, or because of stray local fields created by, e.g., dislocations. These will also behave like "loose spin" degrees of freedom coupling to $\hat{\tau}$.

2. In reality $\vec{\tau}$ will couple to many other 'environmental modes' in the vicinity of the SMM. This includes any nuclear spins in the SMM, coupled via hyperfine interactions, nuclear spins outside the SMM, coupled via magnetic dipolar or possibly transfer hyperfine interactions.[16,17] Also $\vec{\tau}$ will couple to photons (via magnetic dipole and electric dipole couplings) and both extended

Fig. 4 Variation of the effective transverse field Δ_o by application a real transverse field $\vec{H}_0^\perp$ at different angles in the Fe_8 system.

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J. Mater. Chem., 2009, **19**, 1718–1730 | 1721

phonon modes (*i.e.*, magnetoacoustic couplings[17,18]) and local phonons (*e.g.*, vibrons, or impurity-induced local phonons). In a conducting system, $\vec{\tau}$ can also couple to extended electronic excitations in various ways.[17]

3. Finally, an ensemble of SMMs, as in a QIPS, will have various 'stray' couplings between the $\{\vec{\tau}_j\}$, mediated by all the degrees of freedom discussed above, and not included in the 'bare' interactions $U_{ij}^{\alpha\beta}(t)$ which already appear in eqn (3) above. These include 'slow' couplings like those mediated by phonons, in which retardation effects can be important.

Actually there is nothing specific to SMMs about problems like these. Quite generally, in describing a QIPS, we need to include (i) coupling of the qubits to stray environmental degrees of freedom, and (ii) stray couplings between the qubits from these environmental degrees of freedom.

So what kind of model should we really be using for a set of coupled SMM qubits, instead of eqn (3)? The answer proceeds in 2 stages.

(i) Environmental modes. We can divide all the environmental modes into 2 classes (see Fig. 6).[19] First, for all the discrete *localized* modes, like defects, nuclear spins, "loose" spins, localized phonons, etc., we can use a model which couples the qubits to a "spin bath" environment[19] of localized modes. In its simplest form this describes a set $\{\sigma_K\}$ of two-level systems, and we can generalize the bare qubit Hamiltonian in eqn (3) to

$$\hat{H}_{QB} = H_{QB}^0(\vec{\tau}) + H_{SB}^0(\vec{\sigma}_K) + H_{int}^{SB}(\tau_i, \{\vec{\sigma}_K\}) \quad (9)$$

in which the Pauli matrices $\{\vec{\sigma}_k\}$ act on the 2-level systems, and where the spin bath has its own Hamiltonian

$$\hat{H}_{SB}^0(\{\sigma_k\}) = \sum_k \vec{h}_k \cdot \vec{\sigma}_k + \sum_{kk'} V_{kk'}^{\alpha\beta} \sigma_k^\alpha \sigma_{k'}^\beta \quad (10)$$

in which the local fields $\{\vec{h}_k\}$ typically dominate over the rather weak interspin coupling $V_{kk'}^{\alpha\beta}$; and finally the qubit couples to the spin bath *via* the term

$$H_{int}^{SB}(\tau_i, \{\vec{\sigma}_k\}) = \sum_k \omega_k^{\alpha\beta} \tau^\alpha \sigma_k^\beta \quad (11)$$

with couplings $\omega_k^{\alpha\beta}$. More generally we have to couple to a spin bath in which the individual modes have more than 2 levels—for example, to a set of nuclear spins with spin I, having $2I + 1$ levels each. This description may look rather complicated, but note that we can also write $\hat{H}_{QB}$ in the more transparent form

$$\hat{H}_{QB} = H_{QB}^0(\vec{\tau}) + \sum_k \left(\vec{\gamma}_k + \vec{\xi}_k \right) \cdot \vec{\sigma}_k \quad (12)$$

where we define the time-dependent vectors $\vec{\gamma}_k(t)$ and $\vec{\xi}_k(t)$, having components

$$\gamma_k^\alpha(t) = h_k^\alpha + \sum_\beta \omega_k^{\alpha\beta} \tau_\beta(t)$$
$$\xi_k^\alpha(t) = \sum_{k'} \sum_\beta V_{kk'}^{\alpha\beta} \sigma_k^\beta(t) \quad (13)$$

Equation (12) simply says that the k-th bath spin moves in a dynamic field coming from both the qubit (incorporated in $\vec{\gamma}_k(t)$) and the other bath spins (incorporated in $\vec{\xi}_k(t)$). Note that
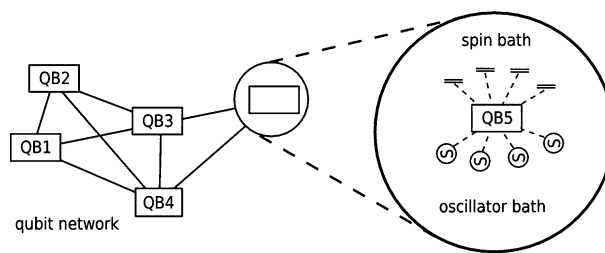

Fig. 6 A network of qubits interacts *via* interactions $U_{ij}(t)$. However each qubit is also interacting with a "spin bath" and an "oscillator bath" (for details see text).

$\vec{\gamma}_k(t)$ is the sum of a static field $\vec{h}_k$ and a dynamic field coming from the qubit. Of course the motion of the k-th bath spin (and all the other bath spins) will also react back on the qubit *via* the interaction $\omega_k^{\beta\alpha}$.

As an example consider the Fe_8 molecule again, in which the core of eight Fe^{3+} spin-5/2 ions couples to over 200 nuclear spins in each molecule (these being a mixture of ^1H, ^2H, and possibly ^{17}O and ^{57}Fe spin 1/2 nuclear spins, as well as some higher spin Br and N nuclear spins). In this system, analysed in detail in ref. 20,21, the $\{V_{kk'}^{\alpha\beta}\}$ are weak internuclear couplings ($|V_{kk'}^{\alpha\beta}| < 10^{-7}K$ even for nearby nuclei), the $\{\omega_k\}$ are hyperfine couplings (with $|\omega_k| \simeq$ 3–4mK for ^{57}Fe nuclei or nearby proton spins) and the $\{\vec{h}_k\}$ include both the weak nuclear Zeeman couplings and a term arising when the Fe_8 giant spin is not flipping between antiparallel orientations when it tunnels.

What about *delocalized* modes, like phonons or photons? These can be handled in a standard way, by coupling the qubit to a bath of oscillators,[22] which now adds an oscillator term

$$\hat{H}_{OB}(\{x_q\}) = \frac{1}{2} \sum_q \left(\frac{p_q^2}{m_q} + m_q \omega_q^2 x_q^2 \right) \quad (14)$$

plus a coupling

$$\hat{H}_{int}^{OB}(\vec{\tau}, \{x_q\}) = \sum_q c_q^\alpha \tau^\alpha x_q \quad (15)$$

to the qubit. In a SMM system, x_q would be *e.g.* the coordinate of a phonon with momentum $\vec{q}$, ω_q its energy, and c_q^α is related to the magnetoacoustic coupling[23] between the SMM and this phonon. This coupling takes the form

$$V_{s\phi} = \sum_q g_{\vec{q}} \hat{O}_S(\vec{S}) \hat{O}_\phi(x_q) \quad (16)$$

where $\hat{O}_S(\vec{S})$ is an operator acting on the giant spin $\vec{S}$, $\hat{O}_\phi(x_q)$ an operator acting on the phonons, and $g_{\vec{q}}$ a coupling function; typically $g_{\vec{q}} = 10$–$100K$ for a SMM. When we then truncate the giant spin Hilbert space down to the qubit space, we get a coupling of the form in eqn (15).

(ii) Stray interactions. Now consider the interaction $U_{ij}^{\alpha\beta}(t)$ between the qubits. Essentially this incorporates all interactions mediated by fields which operate so fast that they can be treated as instantaneous on the timescale of the QIPS. This includes all photon-mediated interactions (including dipolar interactions and exchange interactions). However it does *not* include

phonon-mediated interactions, which are slow—if the time $t_c \sim c_s/L$ taken for phonons to travel across a QIP of size L at velocity c_s is not much less than the timescale of switching or operation of qubits, then we must treat these interactions as retarded, and this can actually lead to decoherence. We ignore this problem in what follows but it is important. This spin–phonon interaction typically has a complicated form—however the main part will be of dipolar form, of strength $\sim g_o^2/\rho c_s^2 r_{ij}^3$, where g_o is the $\vec{q} = 0$ component of $g_{\vec{q}}$ above.

It is essential to distinguish between the short-range and long-range parts of $U_{ij}^{\alpha\beta}(t)$; we write

$$U_{ij}^{\alpha\beta}(t) = K_{ij}^{\alpha\beta} + D_{ij}^{\alpha\beta} \qquad (17)$$

where K_{ij} is the short-range interaction (typically exchange or superexchange), with strength $\sim$50–1000 K for transition metal spins and $\sim$0.1–5 K for rare earths; and D_{ij} is the magnetic dipolar interaction, of strength $\sim V_D/r_{ij}^3$, where $V_D \sim (Sa_o)^2$ K, where $a_o \sim 1$ Å is a microscopic lattice length. The key point is that K_{ij} is only appreciable for nearest-neighbour systems—it falls off exponentially and very fast with distance.

III. Decoherence

Decoherence is the fundamental problem blocking the manufacture of any QIPS. It is considered by many to be an insuperable problem (an opinion we do not share!), as well as being at the very heart of our understanding of quantum mechanics.[24]

For anyone who wants to make a QIPS, decoherence creates a very practical problem—since a QIPS will not work if there is too much decoherence, then in designing one, we need to know how big the decoherence will be. This question has a chequered history. Early calculations of decoherence were far too optimistic—they used oscillator bath models, but at low temperatures most decoherence comes from spin bath environments of localised modes.

Our purpose in this section is (i) to give readers an intuitive feeling for how decoherence works in practise in a system of qubits, and (ii) give some results for decoherence rates which we hope will help to better design a QIPS.

Quite generally, decoherence in the dynamics of some system A is caused by its entanglement with its environment.[24] A key result of quantum mechanics says that if we do not know what the environment is doing, then we must average over all of its possible states when calculating the dynamics of A. But if the environment is entangled with A, then this will "smear out" the phase dynamics of A. Another way of putting this is that if the environment is reacting to the dynamics of A, then it is actually in effect measuring it—and this actually destroys phase coherence in this dynamics.

To see how decoherence works, it is best to divide the discussion between the 3 main mechanisms.

A. Spin bath decoherence

To understand how spin bath decoherence works we need first to see how the bath spins move in the presence of the qubit. Recall that the k-th bath spin moves in a dynamic field $\vec{\gamma}_k(t) + \xi_k(t)$ (see equations (12) and (13)). Since ξ_k is very small compared to $\vec{\gamma}_k$,
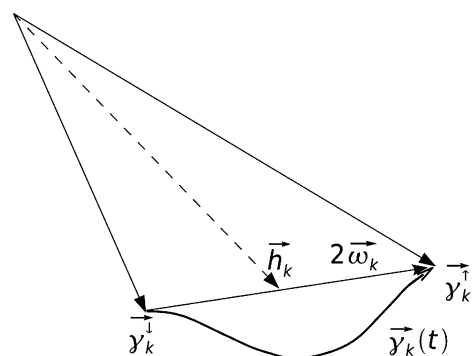

Fig. 7 The k-th bath spin coupled to a qubit has a field $\vec{\gamma}_k(t)$ acting on it, a sum of a static field $\vec{h}_k$, and a part which varies rapidly from $-\omega$ to ω when $\vec{\gamma}_k(t)$ moves between $\vec{\gamma}_k^\downarrow$ and $\vec{\gamma}_k^\uparrow$; this happens when the qubit flips from $|\downarrow>$ to $|\uparrow>$ (a typical path for $\vec{\gamma}_k(t)$ during this flip is shown).

let us begin with $\vec{\gamma}_k$, the net field on the k-th bath spin σ_k; recall it is the sum of the static field $\vec{h}_k$ and the time-varying field from the qubit. Now $\vec{\gamma}_k$ spends almost all of its time in the quiescent states $\vec{\gamma}_k^\uparrow$ and $\vec{\gamma}_k^\downarrow$, associated with the qubit states $|\uparrow>$ and $|\downarrow>$, and given by

$$\gamma_k^\sigma = \vec{h}_k + \sigma\vec{\omega}_k \qquad (18)$$

where $\sigma = \pm$ corresponds to $|\uparrow>, |\downarrow>$ and the vector $\vec{\omega}_k$ is defined by its components $\omega_k^\alpha \equiv \omega_k^{\vec{z}\alpha}$ (see Fig. 7).

However every time the qubit flips (taking a very short "bounce time" $\tau_B \equiv 1/\Omega_o$ to do so), the vector $\vec{\gamma}_k$ moves rapidly between these two quiescent states.

The vector $\vec{\xi}_k$ defining the field from the other bath spins also varies in time, but quite differently. Typically $\vec{\xi}_k$ will look much like a small and slowly-varying random noise source, adding a small "jittering" perturbation on $\vec{\gamma}_k$, to give the total time-dependent field acting on $\vec{\sigma}_k$.

How does $\vec{\sigma}_k$ itself move in response to this, as $\vec{\gamma}_k$ "jerks" back and forth between $\vec{\gamma}_k^\uparrow$ and $\vec{\gamma}_k^\downarrow$? The answer is shown in Fig. 8. At $t = 0$, $\vec{\sigma}_k$ will begin to precess about the initial field $\gamma_k(t = 0)$ (which is, say, $\vec{\gamma}_k^\uparrow$). However as soon as $\vec{\gamma}_k^\uparrow$ jumps to $\vec{\gamma}_k^\downarrow$, then $\vec{\sigma}_k(t)$ must begin to precess around the new field. The resulting motion of $\vec{\sigma}_k$ depends on the exact time sequence of flips of $\vec{\gamma}_k$.

Actually there are two small corrections to this picture. First, there is a small extra "wobble" caused by $\vec{\xi}_k(t)$. Second, we have described the motion of $\vec{\gamma}_k^\downarrow$ as though the jumps between $\vec{\gamma}_k^\uparrow$ and $\vec{\gamma}_k^\downarrow$ were instantaneous, so that $\vec{\sigma}_k$ cannot follow them. However this is not true—although they are sudden, there is still a small perturbation on the dynamics of $\vec{\sigma}_k$.

Now notice a crucial consequence of this picture—it is that the path followed by $\vec{\sigma}_k$ is *conditional* on that followed by $\vec{\gamma}_k$. This means that the 2 systems are entangled—indeed rather strongly so, since the path followed by $\vec{\sigma}_k$ depends more or less entirely on the time evolution of $\vec{\gamma}_k$ (apart from the small perturbation coming from $\vec{\xi}_k$).

Now we can see how a spin bath will cause decoherence in the dynamics of a qubit. If we cannot follow the coupled dynamics of the qubit and each individual bath spin, we must average over the different possible time evolutions of them—a definite time dynamics then gets converted to a time-evolving probability distribution. Thus this entanglement between qubit and spin
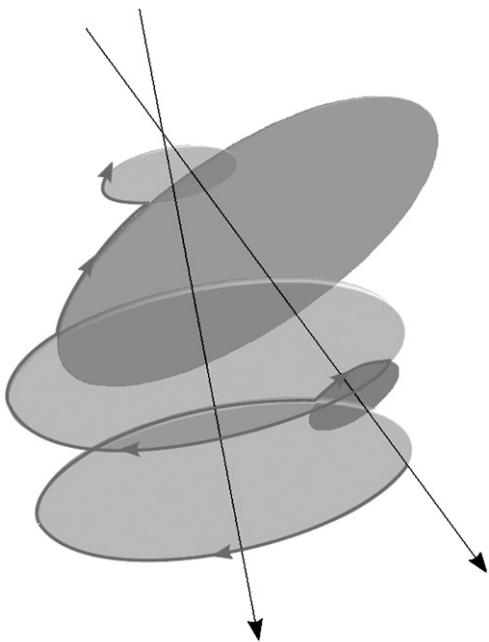
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Fig. 8 A spin qubit flipping between its up and down quantum states also flips the field acting on nearby nuclear spins between two orientations (shown as arrows). The nuclear spins try to precess in this qubit field, but each time it suddenly changes they must begin anew. Thus, the path a nuclear spin vector follows is conditional on the specific trajectory of the qubit, *ie.*, the two are quantum-mechanically entangled.

bath dynamics causes decoherence in the qubit dynamics. In fact we can classify three different decoherence mechanisms here, as follows.

(i) Precessional decoherence. The precessional motion of $\vec{\sigma}_k$ around the time-varying $\vec{\gamma}_k$, shown in Fig. 8, gives the strongest decoherence from a spin bath. Essentially the spin bath is absorbing phase from the qubit, and it turns out that the rate at which the qubit phase dynamics is 'smeared' is roughly proportional to the average solid angle swept out by all of the σ_k together in their precessional motion. A detailed calculation[19,20] gives simple results for the decoherence rate $\Gamma_\phi{}^P$ in two limiting cases:

$$\Gamma_\phi^P \sim 1/2 \sum_k (\omega_k/h_k)^2; \quad (\omega_k \ll h_k) \qquad (19)$$

$$\Gamma_\phi^P \sim 1/2 \sum_k (h_k/\omega_k)^2; \quad (h_k \ll \omega_k) \qquad (20)$$

where $\omega_k = |\omega$ in eqn (18), and $h_k = |\vec{h}_k|$. Note that this "precessional decoherence" (originally called "orthogonality blocking"[25]) does not involve dissipation—no energy is exchanged between qubit and bath, only precessional phase. Thus this decoherence mechanism, by far the most important one coming from the spin bath, is not even dissipative!

The simplest and best-studied example of precessional decoherence is the case of a spin qubit coupled to nuclear spins. Consider the example of Fe_8, already discussed above, where the main contribution to $\vec{h}_k$ is just the Zeeman coupling to the external field, *i.e.*, $\vec{h}_k \sim g_N \mu_N I_k H_0$, where g_N and μ_N are the

nuclear g-factor and magnetic moment. Then from eqn (20) we see that when $H_0 = 0$, the decoherence rate $\Gamma_\phi = 0$ (this is because γ flips then through 180°; such a flip has no effect on the dynamics of $\vec{\sigma}_k$). Decoherence then rises rapidly until reaching a maximum when $h_k \simeq \omega_k$, where ω_k is the hyperfine coupling as before—at this point the bath spins are precessing wildly as the field γ flips between orientations separated by angles $\sim 90°$. Further increase in H_0 then decreases Γ_ϕ, and in the high-field limit Γ_ϕ again becomes very small (in this case $\vec{\gamma}_k^\uparrow$ and $\vec{\gamma}_k^\downarrow$ are almost parallel, so their flipping of τ_z again hardly affects the dynamics). The quantitative details for Fe_8 were worked out in ref. 20.

(ii) Topological decoherence. The above discussion concerned the bath spin dynamics when the qubit was sitting quietly in either $|\uparrow\rangle$ or $|\downarrow\rangle$. But what about when the qubit is actually flipping, and $\vec{\gamma}_k(t)$ is moving rapidly between $\vec{\gamma}_k^\downarrow$ and $\vec{\gamma}_k^\uparrow$? If this flip were instantaneous, there would be no effect on the bath spins—they simply couldn't follow the sudden change. However the time $1/\Omega_o$ taken for $\vec{\gamma}_k$ to flip from $\vec{\gamma}_k^\uparrow$ to $\vec{\gamma}_k^\downarrow$ is actually finite (though still very short). Then elementary time-dependent perturbation theory tells us that the amplitude α_k for the spin σ_k to make an inelastic transition under this sudden change, *ie.*, during the qubit flip itself, is $\alpha_k \sim \pi \omega_k/2\Omega_0$. By the same arguments as before this bath transition must cause decoherence in the qubit dynamics—the bath is actually registering the change in the qubit state (it is in effect performing a measurement), and this transition actually adds a random topological phase to the qubit dynamics.[16] The resulting "topological decoherence" contribution $\Gamma_\phi{}^T$ to the decoherence rate is found to be:[19,16]

$$\Gamma_\phi^T \sim 1/2 \sum_k |\alpha_k|^2 \qquad (21)$$

For most systems this will be very small, since $\omega_k \ll \Omega_0$ as a rule. Thus, for Fe_8, $\Omega_0 \sim 5K$ in low applied fields, whereas most of the $\omega_k < 1mK$; even after summing over ca. 200 nuclear spins, one still finds a very small contribution to decoherence, changing slowly with field as Ω_0 decreases.[20]

(iii) Noise decoherence. The best-known kind of decoherence is that coming from some unknown noisy vector field $\vec{\chi}(t)$ coupling to $\vec{\tau}$. Chemists are very familiar with this in NMR and EPR—it leads to the usual "T_1/T_2 phenomenology", in which the noise causes incoherent relaxation of the qubit energy over a time T_1 and the qubit phase over a timescale T_2. A spin bath also gives rise to this 'noise decoherence'; the weak interactions between the bath spins cause a slowly fluctuating field to act on the qubit, causing T_1 and T_2 relaxation in the standard way.

Notice an interesting consequence of this, which is seen very nicely in experiments on SMMs. Since most of the spin bath dynamics is being driven by the qubit itself (see again Fig. 8), then when the qubit is frozen by an external longitudinal bias field $\varepsilon \gg \Delta$, the bath spins must also largely freeze—without the time-varying field $\gamma(t)$ to drive them, only the very weak $V_{kk'}$ are left to give the spin bath any independent dynamics (*via* the small slowly-varying $\vec{\xi}_k(t)$). Thus we expect T_1 and T_2 to drastically increase when the qubit is frozen. This was seen in very pretty experiments by the Leiden group on the SMM Mn_{12}; they

observed roughly a hundredfold increase in T_1 and T_2 when they pushed the tunneling Mn_{12} molecules off resonance.[26]

Further remarks. An obvious questions which arises here is the following: to what extent are all these decoherence results already incorporated into the T_1/T_2 phenomenology used in experimental chemistry and physics in the last few decades?

We note first that the common practise in the literature (particularly the quantum information literature) of associating decoherence with some "experimental noise" fluctuation source, and then applying standard ideas such as the fluctuation–dissipation theorem[27] to associate this noise with a dissipation, is quite wrong for a spin bath. As noted above, the most important part of spin bath decoherence, *i.e.*, precessional decoherence, simply involves precessional motion—there is no transfer of energy between qubit and bath spins, and therefore no dissipation. Thus there is no classical analogue to decoherence from a spin bath, and no connection between decoherence and dissipation.[16,19,24,25]

Now the "T_1/T_2" phenomenology in NMR is based on the classical Bloch equations. It throws away all the internal phase information in the nuclear spin bath dynamics (including relative phases between spins, entanglement, etc.), leaving only the self-consistent description of a single nucleus in the classical fluctuating mean field from all the other spins (plus any fluctuating fields coming from electron spins, fluctuating external fields, motional narrowing, etc.).

However this T_1/T_2 phenomenology, although it is commonly used in the qubit literature (in discussions of, *e.g.*, Rabi oscillation, or spin echo for a qubit), it is not appropriate to the qubit dynamics.[19,28] To give an idea of what can really happen, in Fig. 9 we show the imaginary part o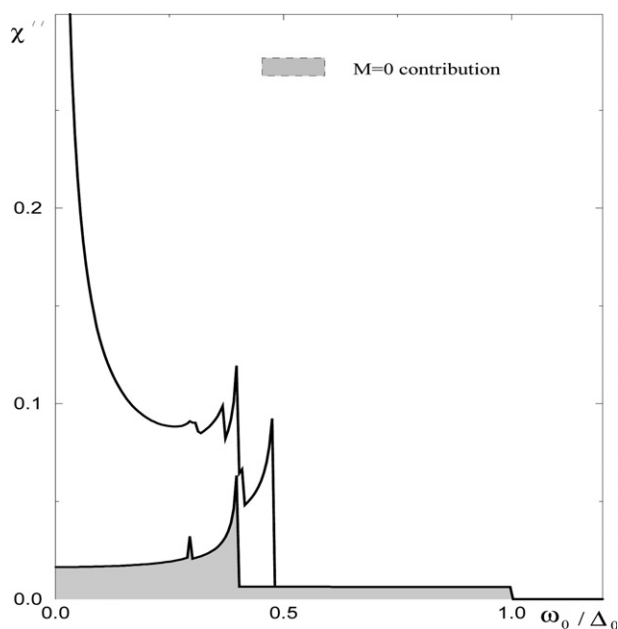f the Fourier transform $\chi_{\uparrow\uparrow}(\omega)$ of the spin correlation function $P_{\uparrow\uparrow}(t)$ for a qubit coupled to a spin bath. This function is the probability that a qubit in state $|\uparrow\rangle$ at the time $t = 0$ will be found there at time t. Thus $\chi_{\uparrow\uparrow}(\omega)$ is the absorption intensity at frequency ω in a qubit resonance experiment. This looks nothing like the Lorentzian expected in the T_1/T_2 phenomenology, and it shows singular peaks which come from the unusual coupled dynamics of qubit and spin bath. These features actually result from decoherence and are not associated with dissipation.

This point is important, because it means that eventually experimentalists working on qubits are going to have to abandon the T_1/T_2 phenomenology in describing their experiments, when spin bath decoherence is important. The phenomenology that will be required needs a whole paper on its own.

B. Oscillator bath decoherence

This has been well covered in other articles[22,29] and books.[30] The theoretical problem is simply formulated—one now couples a qubit to a bath of oscillators, and tries to calculate the dynamics. This "spin-boson" model is well understood.[30] In contrast to the spin bath, there is a quantum–classical correspondence for oscillator baths,[31,32] and a fluctuation–dissipation theorem relating both the dissipative dynamics and the decoherence of the quantum system to the fluctuational "quantum noise" acting on it, coming from the oscillator bath.

Thus we can understand decoherence in the spin-boson model in a fairly simple way. The oscillator bath has two main effects. First, it slows down the qubit, increasing its "inertia", so that Δ, the qubit flip rate, is "renormalized" (*i.e.*, $\Delta \to \tilde{\Delta}$ with $\tilde{\Delta} < \Delta$). Second, it causes dissipation in the "quantum relaxation" of the qubit dynamics, either because the qubit spontaneously emits an excitation (*i.e.*, excites an oscillator from its ground state) or scatters an existing excitation (*i.e.*, stimulated emission—an excited oscillator changes its state, and possibly another one is excited). All the complexity in the qubit dynamics comes from repeated absorption and emission of oscillator excitations.[33,22] Nevertheless the phenomenology is very familiar—one defines a "spectral function"[31] of form

$$J_\alpha(\omega) = \pi/2 \sum_q \frac{|c_q^\alpha|^2}{m_q \omega_q} \delta(\omega - \omega_q) \qquad (22)$$

(where $\alpha = \parallel, \perp$), and the entire dynamics can be calculated in terms of this function, which is familiar from second order perturbation theory or from Fermi's golden rule. It has the form $(V^2/\omega) \times$ (density of states), where $V \equiv c_q^\alpha$ is a coupling constant and ω the energy denominator, and the sum over $\delta(\omega - \omega_q)$ measures the density of oscillator states at ω.

Most of the theoretical work on the spin-boson system has been done for the simple T-independent "Ohmic" form $J(\omega, T) \to \eta\omega$. However most experiments, certainly on qubit systems, are not described by an Ohmic model, for two reasons. First, as already discussed, spin bath decoherence is not at all described by such a model. Second, even without the spin bath, the oscillator bath is often not Ohmic. It certainly will not be if the system is insulating, since for phonons $J(\omega, T)$ depends strongly on T and is a higher than linear power of ω. Only for simple conductors is

Fig. 9 Plot of *Im* $\chi_{\uparrow\uparrow}(\omega)$, the absorption probability described in the text, for a qubit coupled to a spin bath. Without decoherence this would be a sharp line at $\omega/\Delta_o = 1$. The shaded part shows contributions from processes where the spin bath polarisation is unchanged.

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the Ohmic form always valid. For a proper discussion of the different forms of $J(\omega)$, see refs. 17,22,30.

As an example let us again take the SMM. The principal source of oscillator bath decoherence is then the magneto-acoustic coupling to acoustic phonons (for which $J(\omega) \sim \omega^3$). Both quantum relaxation rates[17,18] and decoherence rates[20,34] have been calculated for this interaction. The usual form for the decoherence rate in a transverse field is

$$\Gamma_\phi \sim \frac{|M_{fi}|^2 \, \Delta_o^3}{\pi \hbar^3 \rho c_s^5} \coth\left(\frac{\Delta_o}{kT}\right) \qquad (23)$$

where M_{fi} is the spin-phonon matrix element discussed in section II, ρ the density, and c_s the sound velocity. This expression illustrates nicely the points made above; we have a (matrix element)^2, multiplied by a density of states $\sim\Delta_o^3$, divided by an energy denominator Δ_o, multiplied by a thermal factor $\sim\Delta_o^{-1}\coth(\Delta_o/kT)$. In other words, just the golden rule. A more sophisticated calculation hardly changes this result, simply renormalizing Δ_o. An Ohmic bath would give a completely different result.[17,22] Actually, decoherence from an Ohmic bath is typically very large, which is why in making a QIPS we want to avoid having moving electrons (*ie.*, one should use insulating systems). Of course, this still leaves decoherence from the spin bath.

C. Pairwise dipolar decoherence

We now turn to what may in the long run be the most insidious kind of decoherence—that caused by unwanted long-range interactions between the qubits. There are two kinds of these, viz. (i) interactions like dipolar or (in the case of current-carrying devices) unscreened inductive interactions, which can be treated as instantaneous; and (ii) long-range interactions mediated by slow particles like phonons, which may have a retarded character.

The reason such interactions are so dangerous is that they affect many qubits at a time. Only a few theoretical studies have so far appeared. Aharonov *et al.*[35] argue that concatenated error correction codes can handle long-range interactions, but only just. It is however likely that the model in this paper is over-simplified, since detailed calculations for both insulating systems[34] (where dipolar inter-qubit interactions are important) and conducting systems[36] (where inter-qubit interactions mediated by the electron bath are important) give rather different results. Thus the problem is still open, and we do not give any detailed results for decoherence rates here.

We can nevertheless give a simplified description of what is going on (see Fig. 10). With long-range ($\sim1/r^3$) interactions, it is *always* possible for a given qubit to find resonance with many others in 3 dimensions, whether we want it or not, provided the strength of these interactions exceeds a critical threshold (this result basically goes back to Anderson[37]). Typically for dipolar interactions the resonances will occur over rather long distances. There are really only two ways to get round this problem—first, to use error correction (a topic whose details[6] we have eschewed in this article); and (ii) use a lower dimensional geometry, which drastically reduces the number of qubits that are far apart (compared to the 3d case). Ideally one uses both—in section IV
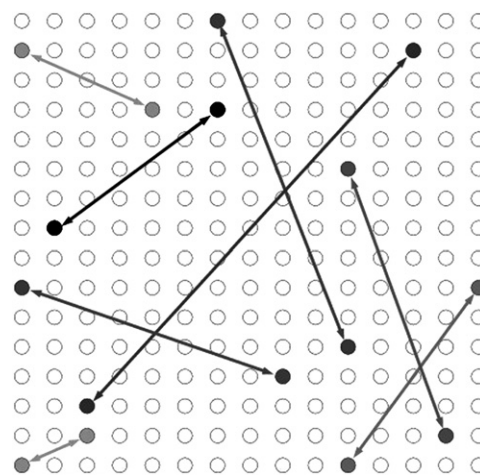

Fig. 10 Two-dimensional spin network, showing resonant pairs of qubits interacting *via* dipolar couplings.

we discuss certain architectures which can reduce the effective dimensionality of the QIPS.

IV.   Design criteria: possible architectures

Let us now use the results given in the previous section to discuss the best way to *make* a QIPS. To recapitulate—we want a system of qubits whose mutual interactions, and the local fields acting on them, can be accurately controlled (or, if they are static in time, are very accurately fixed and can be tuned). We want to be able to write quantum information onto the states of these qubits, do a computation, and then read out the answer. We do not want stray interactions or fields interfering with this, and we certainly want to minimize decoherence caused by interactions with other uncontrolled degrees of freedom. So how can we best achieve all these desiderata?

As advertised in the introduction, we concentrate here on designs for spin QIPS using materials chemistry, *ie.*, 'bottom-up' approaches. The main advantages of such an approach (as opposed to top-down 'nanofabrication' approaches), are:

A1) reproducibility—chemistry uses quantum mechanics to produce absolutely identical molecules or other kinds of spin complex;

A2) size—the qubits and other parts of the architecture are really small, so that few degrees of freedom are involved, and few defects; hence decoherence is reduced and timescales become short;

A3) no moving electrons—moving electrons always cause decoherence. With insulating molecules or other spin complexes one can make a true spintronics system, which only involves spin degrees of freedom.

There are also disadvantages: the main ones are

D1) size—molecular and ionic spin moments are currently too small to be either controlled or examined individually, except in very small numbers. In most QIP algorithms, we need to be able to control, address, and read out the states of individual qubits;

D2) dipolar interactions—as discussed above these are potentially fatal to QIPS—one needs architectures that suppress them. Our task is thus to find designs that use the advantages (A1)–(A3) to their fullest extent, and overcome the disadvantages

(D1) and (D2) as much as possible. In bottom-up designs the main weapons we have are (i) the methods of chemistry, and (ii) a huge variety of potential geometries, *ie.*, possible QIPS 'architectures'. We deal with these in turn.

A. Chemical approaches

At the level of individual ions or molecules, materials chemists are well-placed to deal with the problems of reproducibility and decoherence, at both the nuclear and electronic scale.

(i) Nuclear chemistry. Unless one wishes to use nuclear spins as a QIPS resource (for which see below), then their enormous contribution to decoherence means we simply want to get rid of them. Now while all "odd" nuclear isotopes (*ie.*, with an odd number of protons) have $I \neq 0$, at least one isotope of every even element has $I = 0$. Indeed, in natural mixtures of even-numbered elements, the $I = 0$ isotopes are the most common. Thus we should aim for systems with even-numbered elements only.

Of course, if one aims strictly for even nuclei, the chemical playground is dramatically reduced, and isotopic purification is still typically required. Obvious transition metal choices are Fe (with 2% ^{57}Fe) or Ni (with 1% ^{59}Ni). There are also a number of rare earth candidates. These are either even-numbered (like Nd, Dy, Er, Yb) with a complex mixture of isotopes and the possibility of having only $I = 0$ through costly isotopic purification, or odd-numbered (like Tb, Ho), where $I \neq 0$ but only a single isotope is naturally prevalent. Note however that in this case we deal not with a single rare earth ionic doublet at low energies, but an electronuclear pair of spins—the nuclear spin hyperfine coupling is so strong that one cannot rotate without the other.[38]

An entirely new range of possibilities opens up if we use nuclear spins as part of the QIPS (*e.g.*, in a quantum register). We then must be able to switch on and off the interaction (and hence the information flow) between the nuclear and electronic spins. One way to do this is dynamical—one tunes the electronic and nuclear spin splittings (*e.g.*, with external fields) so that resonant hyperfine-mediated interactions can be switched on and off. Concrete practical designs are needed here—the big stumbling block will be decoherence from dipolar interactions between nuclear spins and remote electronic spins (even if these latter do not partake in the resonant interactions, their dipolar field adds extra dynamic phase to the nuclear dynamics, and can throw them off resonance).

Another possibility is to switch the hyperfine interactions on and off. In spin transition systems the electron spins can be switched on and off without a change in the redox state, using temperature, pressure or light (the LIESST effect,[39] or SOX-IESST[40]/HAXIESST[41] for soft/hard X-rays). If a design based on this effect could be made to work it would be very powerful—one would simply switch off the QIPS when it was not needed, storing information in the nuclear register.

(ii) Electronic chemistry. Undoubtedly one area where chemists can play a big role is in the design of interactions (*ie.*, engineering of effective Hamiltonians), and the preparation of uniform and reproducible qubits.

The first problem then is the design of individual spin qubits. Let us first note that seemingly obvious candidates such as molecular Kondo systems or electrically controlled quantum dots,[10,42,43] while promising, have one very serious drawback—they have an intrinsically high decoherence, as their operation is based on moving electrons.

So let us now consider insulating SMMs and rare earth ions as qubit candidates. A question often asked by molecular chemists is—what kind of crystal field is needed for the spin qubit? As noted earlier, designs in which there is a 'natural basis' for the qubit, created by a 2-well potential, are usually good ones. Many tunneling SMMs and rare-earth ion molecular systems now use this design—the question at issue is how big to make the spin anisotropy energy barrier E_B. One wishes to operate the QIPS at energy scales $\ll kT_c$, where $kT_c \sim E_B/2\pi S$ is the crossover energy to the qubit regime (above T_c, the spin dynamics proceeds by incoherent thermal activation). However at the same time we want to suppress decoherence from nuclear spins and phonons. This imposes competing restrictions: to reduce nuclear spin decoherence one wants $\Delta_o \gg \{\omega_k\}$, where the $\{\omega_k\}$ are the couplings to the spin bath (nuclear spins in this case), but to reduce phonon decoherence one wants Δ_o as small as possible compared to typical phonon energies (whose scale is determined by the Debye energy θ_D). Thus there is a 'coherence window',[20] defined by $\theta_D \gg \Delta_o \gg \{\omega_k\}$, defining a desirable size for Δ_o. Noting that Δ_o is certainly less than kT_c, we can put these various restrictions together as a requirement that $\theta_D \gg E_B/2\pi S \gg kT, \Delta_o \gg \{\omega_k\}$. Thus we would like to have a large magnetic anisotropy and weak hyperfine couplings—and a system that can go to very low temperatures. Certainly the most important requirement here is weak hyperfine couplings. It also helps if θ_D is big and if the spin–phonon couplings are weak (which will happen if the molecule is, eg., nearly spherically symmetric).

If one uses transition ion SMMs based on even nuclei (so as to eliminate nuclear spin decoherence), severe restrictions are placed on the chemical bridging between the spins—one has to discard all the halogens and almost every organic molecule because of their hydrogen and nitrogen nuclear spins. For coordination and short-range bridging, obvious choices are then oxo, tio or oxalate anions, but there are others, like carbonyl, thiocarbonyl or carbide.

Alternatively one can go for rare earth-based molecules. Single lanthanide cations in adequate coordination environments have shown SMM behaviour;[44] and recently, polyoxometalates (POMs) composed completely of W, O and Si have shown crystal fields capable of giving qubit dynamics.[45] This offers exciting new possibilities, as POMs are chemically quite different from the usual SMMs (they have high negative charge, and are stable against oxidation). Two advantages of any rare earth design are (i) the relevant magnetic parameters can be calculated theoretically from their structures and/or extracted from EPR and optical data; and (ii) their strong magnetic signals and hyperfine coupling (when using nuclei with $I > 0$) facilitate their detection and characterization.

Another key requirement is the reduction of disorder to very low levels—this means eliminating defects, dislocations, etc., from the QIPS, and using molecules or other spin complexes that only come in one species (*ie.*, not using systems that have active structural degrees of freedom, various kinds of isomerism, or free rotation about single bonds, or solvents/counterions that can take different positions which are close in energy to each other).

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Let us turn now to the design of inter-qubit interactions. These need to be precisely controlled (whether they are static or dynamic) and inter-qubit dipolar interactions and spin–phonon interactions need to be suppressed. Since both are ∝ the qubit spin moment, one possibility is to have antiferromagnetically ordered spin qubits. The inter-qubit interactions would then vanish much more quickly at long range (for an antiferromagnetic pair, they are $\propto a/r^4$, where a is the separation between the spins). If the spins in each pair are not equivalent (eg., in an antiferromagnetic transition metal dimer where the two metals are either different or have different chemical environments), an external stimulus (e.g. an EPR pulse) will differentiate the $|\uparrow\downarrow>$ and $|\downarrow\uparrow>$ configurations. This way of suppressing dipolar interactions also suppresses the spin–phonon interaction. Important work that has already been done in this direction with dimeric molecular nanomagnets,[46,47,48] including molecules where there is a built-in switch.[47] We would suggest making analogues to these systems in which the dipolar magnetic moments cancel completely while a strong quadrupolar moment remains. Alternatively, heterometallic antiferromagnetic wheels,[49] with $S = 0$, are clearly promising building blocks, and qubit designs for these systems have already been explored.[50]

The most obvious way to implement inter-qubit interactions is to use exchange or superexchange interactions between neighbouring spins. Transition metal-based systems have interactions $\sim O(100 \text{ K})$, making them better than rare earths, where these interactions are typically $\sim O(1 \text{ K})$. If controllable long-range inter-qubit interactions are desired, one can imagine propagating these through reduced carbon nanotubes[51] or POMs.[52] Both can in principle mediate relatively long-range indirect exchange through the delocalized electrons, compared to superexchange, and both can be prepared using only $I = 0$ isotopes. However, they involve moving electrons, a serious source of decoherence; a better way would be to propagate spin signals down a chain of strongly exchange-coupled insulating spins.

B. Geometry, architecture, and fabrication

The actual spatial arrangement of qubits, and the 'read in/read out' probes which couple to them, is quite crucial to the design of a QIPS. There are 3 main issues, viz. (i) the small size of spin qubits based on molecules or other spin complexes means that with current detection/control systems, it is hard to manipulate, read in, or read out the state of a single qubit; (ii) the much larger size of these detection/control systems means that they cannot be 'crowded in' to interact with more than a few qubits at a time; and (iii) the geometrical design of a QIPS will greatly influence decoherence, both from stray fields (e.g., from substrates) and from long-range dipolar interactions.

(i) Geometry and architecture. Current probes (micro-SQUIDs, STM and MFM systems, Hall probes, optical detection and control systems, etc.) are partly dogged by the uncertainty principle—if one is not careful, attempts to probe or control at a length scale of the order a qubit size (ie., a few nm) will have far too destructive an effect on the qubits and their quantum states (thus if photons were used, we would be dealing with soft X-rays!). STM and MFM probes can have a very weak effect, even though their tips are very small—but the rest of the

probe is very big, and there is no obvious way to address many qubits at a time with this technology.

The most obvious way to get round this problem is to use fixed probes of *nm* size, connected remotely to the outside world along one-dimensional connecters. Conventionally one thinks here of wires and moving electrons—conceivably some future nano-SQUID array could do the job. However it seems better to us to use a genuinely spintronic arrangement of interacting spins (e.g., using strongly coupled chains of spins, or possibly a set of nanotubes) to couple into the qubit array. These can themselves be connected to much larger control and read in/read out systems outside the QIPS. As yet there are no concrete designs in this area—it would be useful to have some.

Another possibility, at least in the near future, is to make larger spin-based qubits—a large (e.g., 50×50) spin array (square, hexagonal, linear) of microscopic spins or SMMs, coupled antiferromagnetically. These would interact *via* a few nearest neighbour spins. A further advantage of this design would be obtained if each qubit had no net spin, thereby suppressing dipolar errors. Promising advances here are being made with the synthesis and study of mesoscopic antiferromagnetic grids.[55]

Another question which we find interesting is the way in which both the read in/read out and decoherence problems might be alleviated by using a 'sparse architecture' for the qubits.[56] By this we mean an arrangement of qubits on, e.g., a planar substrate, whose total number does not increase linearly with the area of the system, but more slowly. This allows easier access for probes, and also strongly reduces errors caused by dipolar interactions. Many geometries are possible here, ranging from coupled lines or nanorods of various shapes to 'fractal' patterns on surfaces. The chemistry and physical properties of the substrates will be important in limiting these designs. For example, while dendrimers[57] could be a promising scalable support for sparse architectures, steric hindrance usually induces disorder in their structures, which would cause decoherence.

Finally, let us mention two other interesting alternative designs which could alleviate the architectural problem. The first involves using specific algorithms that avoid single-qubit addressing altogether;[53] only the entire QIPS is addressed, but on multiple occasions after a series of pulses. The other uses molecular cellular automata[54] which only need addressability at edges, thus reducing the addressability problem by one dimension. Both of theses designs suffer because they require a long time to carry out a computation—they can only work if decoherence times are really long.

(ii) Fabrication. This brings us back to the problem of fabrication of these QIPS arrays. The range of possibilities is enormous; we mention just a few. As far as SMMs are concerned, we gave the main desiderata above—the interesting question is what new possibilities would be useful to explore. One is POMs, which have a rich chemistry offering different topologies, sizes, and the ability to encapsulate magnetic metal ions in arbitrary ligand fields and/or host delocalized electrons if desired.[58] As noted above, they can be built entirely using even elements (mainly W, Mo and O). Thus, one could explore "giant" POM wheels,[59] currently about 4nm in radius. It may be possible to build a wheel which (i) is even bigger, (ii) is free from nuclear
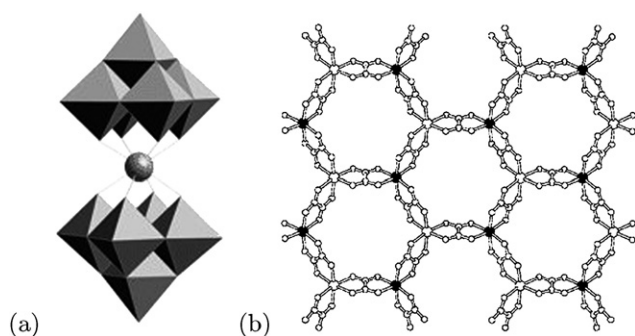
Fig. 11 Some systems that can be synthesized with a small amount of nuclear spins and that could serve as hardware for qubits (see text for details). (a) Single-molecule magnet based on a single lanthanide ion. (b) Bidimensional "honeycomb" oxalate network.

spins (current designs contain many water molecules), and (iii) has the magnetic network we want inside. Alternatively, with an array of STMs, one could chemically prepare a self-assembled monolayer of POMs or fullerenes, and inject a single electron on each molecule directly under each tip. The chemistry would be quite easy, and avoids nuclear spins, since fullerenes and POMs are based on even-numbered elements. The main problems would be (i) electron delocalisation in the molecules introduces new paths to decoherence, and (ii) this scheme would shift part of the difficulty from the chemistry to the nanoengineering.

We also note that a way to prepare antiferromagnetic 2-D lattices which are poor in nuclear spins and have two distinct sites is to use bimetallic honeycomb oxalate layers;[60] see Fig. 11. One of the metals will always carry a nuclear spin, but the other can be clean if one so chooses. They have no water, but do require a nearby cationic layer, to compensate their own anionic charge. This cationic layer could be Ca^{2+}-based.

Finally, we emphasize the care required in designing substrates. They will cause strong decoherence if there are any 'spin bath' defects (dangling bonds/free radicals, or charge defects, or paramagnetic spins, or nuclear spins) which can couple to the qubits. Solving this will not be easy—getting rid of nuclear spins in the substrate may be the hardest task of all. POMs, among a vast variety of molecules, have been organized bidimensionally in different ways, including Langmuir–Blodgett films and through covalent modification of the surface. Of course, usually these ways make extensive use of elements with an odd number of protons, so potentially the cleanest way would be to use self-assembled monolayers (SAMs) on an adequate substrate. Highly ordered pyrolytic graphite[61] and silicon[62] have been demonstrated to support SAMs of—among other chemical species—different POMs, and are all free from nuclear spins. Quartz would be a good insulating substrate, but the preparation of POM SAMs on quartz usually involves organic molecules to provide for a positive charge,[63] which defeats the purpose of choosing a nuclear-spin-free substrate.

V. Concluding remarks

The international effort to make a QIPS has assumed very large proportions, but building a QIPS will obviously not be easy—the main problem, as we have seen, is to suppress decoherence, particularly from nuclear spins and dipolar interactions. The use of insulating atomic or molecular scale spin qubits offers important advantages—reduced decoherence, and with appropriate care, high reproducibility. We have explored herein a large number of design strategies for building a QIPS. It seems likely to us that experimental efforts to gain control of decoherence and make systems of multiply entangled spin qubits will succeed in the next few years. At this point it should be possible to devise realistic architectures for large scale quantum information processing, and we anticipate that chemical considerations will play a large role in these efforts.

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