A BRIEF INTRODUCTION TO SINGLE MOLECULAR MAGNETS

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Abstract. Single Molecular Magnets(SMM), has attracted much interest. Their large spin and quantum behavior at a mesoscopic scale, indicates rich physics behind these unusual phenomena as well as prospective application values. In this article, quantum tunneling magnetization (QTM), the origin of the magnetism in SMM, is discussed. Then it is followed by two typical cases: integer spin SMM and 1/2 spin SMM.

Introduction

Nanoclusters bridges between the classical world we are used to, and the brave new quantum world. Many quantum effects were observed at these mesoscopic-scale systems, like quantum phase interference and coherence, and quantum tunneling magnetization, which would be discussed later. A kind of magnetic nanoclusters, called Single Molecular Magnets(SMM), have attracted much interest in application already. Large spin alone has provided application in biology like sharp image in MRI[1] or ion-exchange purification of proteins[2]. Their small size and intrinsic memory effect provides possible ways for highly integrated devices[3]. Moreover, due to their amazing property of having so many particles entangled, and even the ability to resume entanglement via self-organization, it is very likely that they might be the suitable material to realize quantum computing[4].

Theoretical interest arises for these promising materials which have quantum behavior beyond microscopic world. Ideally, using Heisenberg model containing all the spins in the clusters would give us everything. However, this is too complicated. A single cluster does not have as good periodicity as a bulk crystal. Neither does it have large enough scale to ignore surface effects[5]. The interactions between the spins are so complex that in some cases not only their magnitudes, but their signs as well differs from one experiment to another[6]. On the other hand, many easier approximations have been proposed and prove to be helpful. For example, single spin model is successful in explaining the the behavior of integer-spin clusters. This is a benefit from strong coupling within cluster.

Two kinds of clusters would be briefly introduced as examples. One is the family of integer-spin clusters, such as Mn_{12} and Fe_4. This kind of single molecule magnet has large susceptibility and have a characteristic staggered hysteresis, indicating a large spin, the components of which are quantized. The other kind is 1/2-spin big molecules like V_{15}. Single spin model fails to

explain and predict the magnetic behavior of these clusters. More detailed modeling is needed to describe them.

Origin of Magnetism

Before investigating these interesting magnetic materials, a brief look at how a piece of material got magnetized would be helpful. The origin of magnetism is the angular momentum of charged particles. For metal, it is electron spin. How these spins are aligned gives the magnetic properties of the material.

The simplest case is near-independent electron gas. Without external field, the spins have equal chance for all allowed directions, and therefore the total magnetic dipole moment is zero. When external field is applied, the degenerated energy level splits and the spins are distributed according to fermi distribution. The metal responds to external field by polarized in the same direction of the field. This is known as Pauli paramagnetism.[7]

However, as all the spins has nothing to do with each other, it is impossible to explain spontaneous magnetization. Heisenberg solved this problem by applying Pauli exclusion principle, introducing an exchange interaction term in the Hamiltonian, so that spin at each site is related with its nearest neighbor. Later, the exchange interaction was categorized into different types depending on the construction of crystal, shell structure, as well as the presence of conducting electrons. Despite these differences, the exchange interaction explains long-range ordered magnetism. At sufficiently high temperature, thermal energy overcomes the coupling interaction, and the material shows paramagnetic behavior. [7]

When the material goes down to nanoscale, more interesting behaviors were observed. These results from the anisotropy of the cluster.

Superparamagnetism is one of the interesting properties. It keeps to be paramagnetic below Curie Temperature, but with high susceptibility. Moreover, there's a frequency-dependence of its ac-susceptibility. At temperatures lower than Curie Temperature, the thermal energy is insufficient to break all magnetic order. However, due to the small size, the thermal energy can still change the direction of the entire crystalline, while the atoms within the crystalline tend to an ordered alignment along a preferred axis, so-called easy axis. Thus, the cluster can be treated as a single macrospin. But this size cannot go down to an infinitely small scale, or the temperature for superparamagnetism would be lowered. This is known as the superparamagnetism limit. In other words, it is a limitation of the integration of spintronic devices. The frequency response of superparamagnetism is described by the Nèel-Arrhenius equation:

$$\tau = \tau_0 exp(\Delta E/(k_B T))$$

Where τ is the average length of time the cluster takes to flip direction randomly, τ_0 is the characteristic time of the material. ΔE is the magnetic

anisotropy energy, a barrier between the two energy minimum (direction along easy axes) through a saddle point (along a hard axis). Moreover, this indicates intrinsic remnant, which is essential for application as magnetic memory. In magnetic nanoclusters, τ is usually as large as one or two months.

Quantum Tunneling Magnetization

The large spin of the cluster is caused by quantum tunneling magnetization, which is revealed by steps in hysteresis. [8].

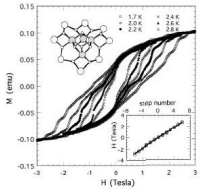


FIGURE 1. Staggered hysteresis of Mn_{12}[8]

Due to anisotropy, the energy landscape of the cluster is viewed as two wells of depth m linked by a barrier, representing from parallel to the easy-axis to antiparallel, through a hard axis. As external field is applied, the formerly degenerated ground state split. The levels in the well of positive spin rises while negative lowered. When two energy levels in the wells match, resonance tunneling occurs. The system tunnels from the left well to the right, and then spontaneously decays to the ground level.

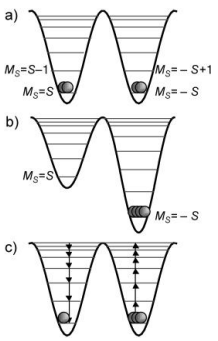


FIGURE 2. Energy level of an anisotropy cluster[9]

The Hamiltonian of an anisotropic cluster can be written as

$$H = H_0 + H'$$

where

$$H_0 = -DS_z^2 - g\mu_B S \cdot \mathscr{H}$$

Here D is a parameter representing the axial anisotropy of the cluster and H' includes all the perturbation terms that does not commute with S_z. Suppose H' is so small that it can be casted away when calculating the external field $\mathscr{H}$ at which energy of the state $S_z = m$ coincides with the state $S_z = -m + n$. For simplicity, suppose $\mathscr{H}$ is along the easy axis.

$$\mathscr{H} = -\frac{nD}{g\mu_B}$$

This means, to change the magnetization by one unit, the external field has to increase by $\frac{D}{g\mu_B}$. And it is in agreement with the steps in the hysteresis.

In Friedman's paper[8], the influence of temperature is also discussed. At low temperature, initially the system in the degenerated ground state in the wells. So in external field, only the transition from the ground state in the left well to the levels in the right well occurs. But when thermal excitation occurs, particles are distributed on different levels. As a result, a higher transition rate is observed at higher temperature. And it is also found that below a threshold temperature, pure quantum tunneling takes place. [8] On the other hand, if the temperature exceeds a *blocking temperature*, thermal excitation is sufficient to get the cluster out of the wells, and as a result, paramagnetism occurs within the cluster.[9]

The double-well model also helps to calculate the relaxation time. Eventually the distribution reaches a thermal equilibrium. The characteristic relaxation time τ_0 is related to the transition rate from the right well to the left one. Spin-phonon interaction and the barrier ΔE matters. ΔE equals to $-DS^2$ for integer spins and $-D(S^2 - 1/4)$ for half-integer spins. Thus, the larger the spin value, the higher the barrier, the longer the relaxation time, and the better the intrinsic magnetic memory. And that's probably one reason why magnetic clusters of large spin attracts much interest.[9]

So far, we have discussed H_0, the term that commutes with S_z. No actual tunneling would occur without a transverse term. H' describes the anisotropy in the xy-plane. A commonly used form of H' is

$$H' = E(S_x^2 - S_y^2) = \frac{E}{2}(S_+^2 + S_-^2)$$

If E is positive, the energy cost to align along the x-axis is higher than y-axis. So the spin would tend to stay away from the x-axis. H' mixes levels of $S = M$ and $S = M \pm 2$. as a result, transition would occur between these states.[9]

However, due to the perturbation, there's a gap open Δ at the otherwise crossing states, which prevents tunneling. Thus tunneling is only possible when avoid crossing the gap is possible. The probability is given by the Landau-Zener formula:

$$P = 1 - exp(-\pi\Delta^2/4\hbar\mu_B r)$$

where r is the sweeping rate of the external field. This explains why for different sweeping rates, there's different hysteresis. When sweeping rate is too low, tunneling is not likely to happen. On the other hand, when the rate is too high, time is not long enough and the step is said to be "frozen". More interestingly, the gap Δ quenches when external field meets certain conditions. If external field is applied parallel to a hard axis, the splitting gap quenches when external field satisfies

$$H_x(n) = (2n+1)\sqrt{E'(E'+D')}$$

where

$$E' = E/g\mu_B, D' = D/g\mu_B$$

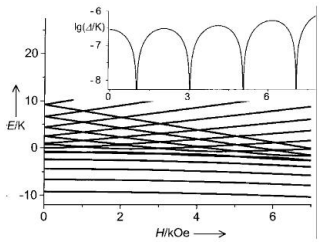


FIGURE 3. Gap quenches with Magnetic Field[9]

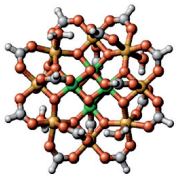
If H_x is applied in the presence of a field parallel to the easy axis, then parity plays a role. There would be a shift when n is odd.[9]

Concluded from all above, QTM of an SMM is described as spin captured in two wells. With properly applied field, the energy levels in two wells meet and the gap by transverse terms was quenched, tunneling happens, which leads to magnetization. Many factors accounts for the tunneling efficiency: the barrier height determined by anisotropy of the cluster, the distribution in levels influenced by temperature, energy level and gap quenching related to external sweeping field.

Integer-Spin Clusters

$[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12} \cdot 2CH_3COOH \cdot 4H_2O]$ (referred to as $Mn_{12} - ac$ or simply Mn_{12}), is the very first SMM synthesized by Lis in 1980[10]. Thermally assisted QTM was also first observed in measuring the hysteresis at low temperature of this cluster[8]. It is the most widely studied single molecular magnet.

The twelve Mn molecules in the cluster is distributed in an D_{2d} symmetry of which the symmetry axis is parallel to the crystallographic c-axis. Mn^{3+} (spin 2) forms an external octagon, surrounding the tetrahedron formed by Mn^{4+} (spin 3/2). In the ground state all the Mn^{3+} are spin



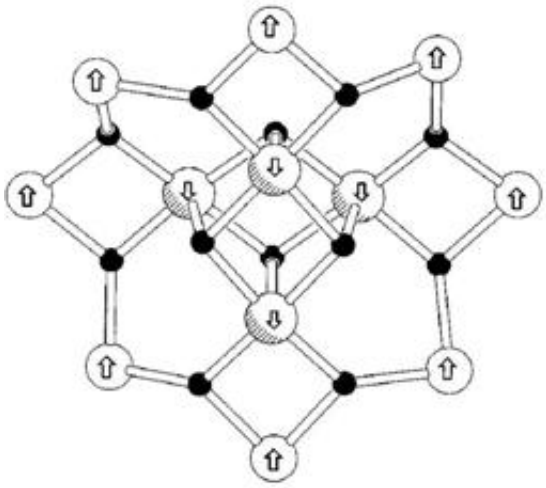


FIGURE 4. Mn_{12}[11][12]

up and Mn^{4+} spin down, and total spin S = 10[13]. Unlike the easier case discussed in the last section, now the cluster has a tetrahedron symmetry instead of one hard axis and one intermediate axis. In other words, there're no quadratic but quartic transverse terms and both terms of S_z.

$$H = H_0 + H'$$

where

$$H_0 = -DS_z^2 - BS_z^4 - g\mu_B S \cdot \mathscr{H}$$
$$H' = \gamma(S_+^4 + S_-^4) + H_{unknown}$$

All the parameters can be obtained by fitting the HF-EPR(High Frequency - Electron Paramagnetism Resonance) spectra. $H_{unknown}$ is very small compared to other parts of the hamiltonian. However, it is not trivial. It has to contain some low odd powers of the S_+, S_- operators. In experiments, transmissions between the odd level and even level are observed.[12][14]

However, Mn_{12} is not a perfect material for application and theoretical study. As mentioned above, it has a tetragonal symmetry and H' starts with $S_\pm^4$, unlike lots of its alternatives that are easy to solve explicitly such as Fe_8, Fe_4, etc.[5] Moreover, it is easily influenced by the surrounding. For application, crystals or layers consisting of several of these molecules should be used, and these molecules have to be attached to certain surfaces, especially when, for example, they were used as junctions. Mn_{12} is quite disappointing in that they are not very well isolated. For example, due to comparatively strong intermolecular interaction, it is hard to observe a crossover from thermally assisted tunneling to pure quantum tunneling of Mn_{12}. Only by increasing the distance between Mn_{12} molecules by replacing some group, pure quantum tunneling was observed.[15]

Fe_4 is one of the most promising SMM in many alternatives for Mn_{12}.[16]

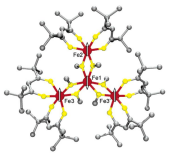


FIGURE 5. Fe_4 [17]

The four Fe^{3+} ions are placed at the vertices and center of a triangle, giving a total spin of 5 at ground state. If the molecule shows an ideal D_3 symmetry, the H' term in the hamiltonian would be still tricky. Fortunately, $Fe2$ differs from the two $Fe3$ ions, and the system is of C_2 symmetry instead. Thus, we can safely apply the form of $H' = \frac{E}{2}(S_+^2 + S_-^2)$ and solve the energy levels using perturbation theory.[17]

Besides the neatness in theory, experiments have revealed many advantages of Fe_4 over Mn_{12}. Main advantage is stability. Either exposure to intense photon flux or attaching to a metal surface, Fe_4 molecule is less likely to loss its symmetry than Mn_{12}. Hysteresis has been found even at the first layer of Fe_4 at the metal surface. Moreover, tunneling efficiency in Fe_4 is significantly higher. On the other hand, due to lower anisotropy barrier, blocking temperature of Fe_4 is quite low, and near zero field magnetic reminisce is small. These are main challenges for application of this SMM and has been intensively studied. For example, experiments on several alternative ligands in the cluster successfully adjusted the anisotropy barrier while maintain the symmetry.[16][18]

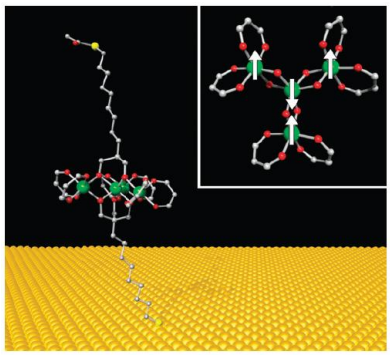


FIGURE 6. Fe_4 cluster Attached to Gold Surface[18]

As shown above, the large-integer-spin clusters are very promising while there's still much to do before wide application. Main challenges includes relaxation properties and stability.An ideal molecular magnet should have

a large enough barrier to prevent lost superparamagnetism at zero field. A long relaxation time is required. Also, it should be stable in environment, hard to be distorted by other clusters, metallic surfaces, or other source of external field such as electromagnetic wave flux.

1/2-Spin Cluster

So far, the theory and experimental results for integer-spin clusters are briefly introduced. There're another large family in the magnetic big molecules with only 1/2 spin. According to the double-well model discussed above, the anisotropic barrier of 1/2 spin molecules should be low. Moreover, the gap splitting which prevents tunneling is high. Large-spin model cannot be applied in such systems. Here, the V_{15} cluster is taken as an example.

FIGURE 7. V_{15} and its Hysteresis[19]

The V_{15} cluster consists a central triangle between two hexagons. The hexagons are coupled by antiferromagnetic interactions. The spins of the hexagons are canceled, and only spins in the triangle is accounted in simplified hamiltonian.[22]

$$H = -J_0 \sum_{i,j=1(i<j)}^{3} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{ij=12,23,31} \mathbf{D}_{ij}(\mathbf{S}_i \times \mathbf{S}_j) + A \sum_{i=1}^{3} \mathbf{I}_i \cdot \mathbf{S}_i + g\mu_B \mathbf{H} \sum_{i=1}^{3} \mathbf{S}_i$$

The first term describes the exchange interaction between the spins. Due to long distance between the three spins (about 10 Å), direct exchange is unlikely. Instead, they are coupled through interactions with the hexagon layers, which are strongly coupled by antiferromagnetic interactions. The second term results from anisotropy. Third term in the hamiltonian describes the interactions between the spins and nuclear spin of protons in the environment, which reduces coherence time in the cluster. The last is Zeeman splitting term. The ground state is spin 1/2.[20][22]

Magnetization of V_{15} cluster is equivalent to how this two-state system

change from one state to the other. Use Landau-Zener formula we know the probability to cross the gap Δ_0 equals to $P = 1 - exp(-\pi\Delta_0^2/4\hbar\mu_B r)$. However, unlike the case of large spin, where splitting Δ_0 is small ($\Delta_0 \ll k_B T$), in this case phonon plays a significant role in transition. The system needs to dissipate energy from the environment. Phonons of energy $h\omega \approx \Delta_0$ would be absorbed. When temperature is low, phonons of frequency ω is depleted and transition is prevented. This is known is *"phonon bottleneck"*. As a result, the system stays in one state and magnetization is kept.[19][21]

1/2 spin large molecules need more complicated model to describe. Due to low barrier and small susceptibility, they are not likely to be applied in large-integrated memory design like Mn_{12} and Fe_4. However, they are intriguing not only because the theoretical implication of entanglement of many atoms, but also possible application in quantum computing. V_{15} showed long coherence time. Moreover, by choosing organic ligands, it can even resume entanglement[22]. With these interesting properties, 1/2 spin SMM would probably contribute as much as their large spin relatives in the age of spintronics.

Summary

In conclusion, at nano-scale, quantum effects plays a significant role in magnetization of these clusters. As a result, these systems are more interesting and promising than their bulk counterparts.

The double-well model describes integer-spin SMM quite well but fails at 1/2-spin clusters. EPR and SQUID are helpful means to investigate these systems experimentally. However, more efforts are needed to formulate a neat theory to describe them, besides fitting and matching the spectrum and obtaining empirical coefficients.

For application, although still a long way to go, these interesting materials have already showed their potential. Fe_4, as an example of large integer spin cluster, is promising in high-integration memory design. It has comparatively large susceptibility and adjustable barrier. It is able to retain magnetization and anisotropy. Half-spin large molecules are of good application potential, too. V_{15}, with its ability to keep relatively stable entanglement, might probably lead to the realization of quantum computing.

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