Dark States and Coherent Control of Spin States in Molecular Magnets

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We propose a scheme to realize coherent control of spin state of molecule magnet, Ni\(_4\). We introduce transverse magnetic fields with special frequencies. When the frequencies of transverse magnetic fields match in some conditions, we obtain dark states in Ni\(_4\) molecules. Through adjusting the magnitude of magnetic fields, we can obtain any arbitrary superposition of the two ground spin states of Ni\(_4\) molecules.

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The dark state is a specific coherent superposition of ground states that is immune to further excitation due to destructive quantum interference. It has played an important role in studies of a number of coherent phenomena in physics such as electromagnetically induced transparency, coherent population trapping, lasing without inversion, slow propagation of light in a medium, optical information storage, and so on.

Coherent population transfer is another application of dark states. When the dark states condition is met, via coherent population transfer, one can produce excitation between states of the same parity, for which single-photon transitions are forbidden for electric dipole radiation, or between magnetic sublevels.

Recently, molecular magnets have received much attention because of observed quantum features at the mesoscopic level and their potential uses in magnetic storage and quantum computing. Leuenberger and Loss have proposed a scheme to realize Grover’s algorithms in molecular magnets such as Fe\(_8\) and Mn\(_{12}\). Hou et al. have suggested to perform CNOT operation in dimer of molecular magnets, [Mn\(_4\)]\(_2\). In this paper, we propose a scheme to realize dark states in molecular magnet Ni\(_4\), so that we can obtain an arbitrary superposition of the two spin states of Ni\(_4\) molecule. Therefore the coherent control of spin states of molecular magnets is realized. [Ni(hmp)(t-BuEtOH)Cl]\(_4\), refereed to as Ni\(_4\), consists of four Ni\(_{II}\) (spin 1) magnetic ions and oxygen atoms at alternating corners of a distorted cube, with S\(_4\) site symmetry. Ferromagnetic exchange interactions between the Ni\(_{II}\) ions lead to an S = 4 ground state at low temperature.

The corresponding Hamiltonian of Ni\(_4\) molecule is given by

\[ H = H_0 + H_1. \]

Here \(H_0\) is the Hamiltonian without the external field. It can be written as

\[ H_0 = -D\hat{S}_z^2, \]

where \(D\) is the axial anisotropy constant and \(\hat{S}_z\) is the z component of spin operator. \(H_1\) is the Hamiltonian due to the interactions with the applied magnetic field

\[ H_1 = -g\mu_B\mathbf{B}\cdot\hat{\mathbf{S}}, \]

where \(\mu_B\) is the Bohr magneton, \(g\) is the electronic g-factor, \(\hat{\mathbf{S}}\) is the spin operator, and \(\mathbf{B}\) is the applied magnetic field.

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Each Ni$_4$ molecule can be modelled as a ‘giant spin’ of $S = 4$ with Ising-like anisotropy. Every eigenstate of Ni$_4$ can be labelled by $|m\rangle$ with $m = 4, 3, \ldots, -4$. With the projection operator $|m\rangle\langle m|$, the Hamiltonian without the applied external field can be written as

$$H_0 = \sum_m \hbar \omega_m |m\rangle\langle m|,$$

where $\omega_m = -m^2 D/\hbar$.

The transverse magnetic fields described by the first part in Eq. (5) rotate clockwise and produce left circularly polarized $\sigma^-$ photons. Absorption (emission) of $\sigma^-$ photons gives rise to $\Delta m = -1 (\Delta m = +1)$ transitions of spin states. While the transverse magnetic fields described by the second part in Eq. (5) rotate anticlockwise and produce right circularly polarized $\sigma^+$ photons. Absorption (emission) of $\sigma^+$ photons gives rise to $\Delta m = +1 (\Delta m = -1)$ transitions of spin states.
There is a key point needed to mention. In order to eliminate the excitation states in the process, we choose the special frequencies of the transverse magnetic fields with appropriate detuning from the gaps between spin states. Here we choose the frequencies \( \nu_i(i = -4, -3, -2, -1, 1, 2, 3, 4) \) of the transverse magnetic fields far-detuning from energy gaps of spin states, such as \( \omega_3 - \omega_4 - \nu_4 = 3\Delta, \omega_2 - \omega_3 - \nu_3 = -\Delta, \omega_1 - \omega_2 - \nu_2 = -\Delta, \omega_0 - \omega_1 - \nu_1 = -\Delta, \omega_0 - \omega_3 - \nu_3 = -\Delta, \omega_0 - \omega_4 - \nu_4 = 3\Delta \) and \( \nu_i = \nu_{-i} \) (\( i = 1, 2, 3, 4 \)), where \( \Delta \) is a finite detuning. The detail of the choosing of the frequencies \( \nu_i \) is shown in detail in Figure 3. In Reference [12], measured EPR spectra on the Ni4 molecules reveal that values of \( D \) are in the range of 0.72–1.03 K. So, the energy gaps between different spin states are \( \sim 10^{-23} \) J. We estimate that the frequencies of the transverse magnetic fields are in the range of 100–700 GHz.

Next we calculate the quantum amplitudes for the transitions induced by the time-dependent transverse magnetic fields by evaluating the S-matrix perturbatively. The S-matrix can be expanded in the perturbation series in power of the interaction Hamiltonian \( H_1^I(t) = e^{iH_0t/h} H_1^I(t)e^{-iH_0t/h} \) as \( S = \sum_{n=0}^{\infty} S^{(n)} \). The \( n \)th-order perturbation series of S-matrix is expressed by

\[
S^{(n)} = \left(-\frac{i}{\hbar}\right)^n \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t_2} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_{n-1} H_1^I(t_1) H_1^I(t_2) \cdots H_1^I(t_n). 
\]

In the \( H_0 \) representation, the S-matrix is expressed by \( S_{\beta\alpha} = \sum_{n=0}^{\infty} S^{(n)}_{\beta\alpha} \), which means the transition amplitude from state \( \alpha \) to state \( \beta \). After a straightforward calculation, we find that the perturbation terms below the fourth order vanish. We also obtain the nonzero fourth order perturbation terms as follow,

\[
S_{0,4}^{(4)} = \frac{-i e^{-i(\phi_0 + \phi_3 + \phi_4)} \prod_{i=1}^{4} \Omega_i^{(4)}}{96\Delta^3} \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t_2} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_{n-1}, 
\]

\[
S_{0,4}^{(4)} = \frac{-i e^{-i(\phi_0 + \phi_2 + \phi_3 + \phi_4)} \prod_{m=-4}^{-1} \Omega_m^{(4)}}{96\Delta^3} \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t_2} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_{n-1}. 
\]

where \( \Omega_i = g\mu_B B_i/\hbar \) (\( i = -4, -3, -2, -1, 1, 2, 3, 4 \)). The higher order perturbation terms are negligible compared with \( S_{0,4}^{(4)} \) and \( S_{0,4}^{(4)} \), so we shall not consider the contribution of the higher order perturbation terms in our approximation.

We can interpret the above perturbation series of S-matrix as the below explanation. Because we choose the appropriate frequencies of the applied transverse magnetic fields with detuning, the transition rates between some spin states are so small that they can be neglected. Only the transitions between spin states \( |4\rangle \) and \( |0\rangle \) and between spin states \( |-4\rangle \) and \( |0\rangle \) are obvious since the frequencies of the applied transverse magnetic fields match the gaps of these spin states in four-photon process as shown in Figure 4. These transitions are four order processes, i.e. when the transitions happen, four photons are absorbed or emitted. If the molecules only occupy the spin states \( |4\rangle \) and \( |-4\rangle \) initially, so, after the applied transverse magnetic field are added, only the populations of the spin states \( |4\rangle \) and \( |-4\rangle \) and \( |0\rangle \) are nonzero. Therefore, Ni4 molecule can be considered as a three-level atom. Suppose that we have an effective Hamiltonian \( H_{\text{eff}}^I \) in the interaction picture about the three-level atom model and that the S-matrix of it is equal to that of \( H_{\text{eff}}^I \). Thus, with this approximation, we obtain the effective Hamiltonian in the interaction picture as,

\[
H_{\text{eff}}^I = -\frac{\hbar}{2} \Omega_a(e^{-i\phi_a}|0\rangle\langle 4| + e^{i\phi_a}|4\rangle\langle 0|) + \Omega_b(e^{-i\phi_b}|0\rangle\langle -4| + e^{i\phi_b}| -4\rangle\langle 0|) 
\]

where \( \phi_a = \sum_{m=1}^{4} \phi_m \) and \( \phi_b = \sum_{m=-4}^{-1} \phi_m \); \( \Omega_a \) and \( \Omega_b \) are the effective Rabi frequencies written as

\[
\Omega_a = \frac{\prod_{i=1}^{4} \Omega_i}{48\Delta^3}, 
\]

\[
\Omega_b = \frac{\prod_{m=-4}^{-1} \Omega_m}{48\Delta^3}. 
\]

We consider the Ni4 molecule as a three-level atom described by the effective Hamiltonian \( H_{\text{eff}}^I \). For convenience, here we set \( \phi_b = 0 \) and \( \phi_a - \phi_b = \pm \pi \). It is straightforward to verify that the following
combinations of spin states $|4\rangle$, $|-4\rangle$, and $|0\rangle$ are eigenstates of this Hamiltonian $H$:

$$|\Psi_+\rangle = \frac{1}{\sqrt{2}}(|0\rangle - \sin \theta |4\rangle + \cos \theta |-4\rangle),$$

$$|\Psi_0\rangle = \cos \theta |4\rangle + \sin \theta |-4\rangle,$$

$$|\Psi_-\rangle = \frac{1}{\sqrt{2}}(|0\rangle + \sin \theta |4\rangle - \cos \theta |-4\rangle),$$

where $\cos \theta = \frac{\Omega_b}{\sqrt{\Omega_a^2 + \Omega_b^2}}$, $\sin \theta = \frac{\Omega_a}{\sqrt{\Omega_a^2 + \Omega_b^2}}$; $\theta$ is mixing angle. The corresponding eigenvalues are $E_+ = \pm \frac{\hbar}{2} \sqrt{\Omega_a^2 + \Omega_b^2}$, and $E_0 = 0$. Here, the wave function $|\Psi_0\rangle$ is the so-called dark state. From Eq. (13), we can see that in the dark state the populations of the spin states $|4\rangle$ and $|-4\rangle$ do not vary with time and no excitation to the spin state $|0\rangle$ happen. The population is trapped in the lower spin states. Although the transverse magnetic fields exist, there is no absorption due to the destructive quantum interference between the two transitions.

When the Rabi frequency $\Omega_b$ is nonzero and $\Omega_a = 0$, i.e. the mixing angle $\theta = 0$, the spin state $|4\rangle$ is right the dark state $|\Psi_0\rangle$. In this condition, the gaps between the dark states and the eigenstates $|\Psi_+\rangle$ and $|\Psi_-\rangle$ are $\pm \frac{\hbar}{2} \Omega_b$, which are nonzero. We choose the spin state $|4\rangle$ as the initial state. At first we adiabatically increase $\Omega_b$ from zero to a finite value and keep $\Omega_a$ zero. Then we change the Rabi frequencies $\Omega_a$ and $\Omega_b$ as we want via varying the amplitudes of the transverse magnetic fields, so the mixing angle $\theta$ will vary continually with time. Therefore the state can be written as

$$|\Psi_0(t)\rangle = \frac{\Omega_b(t)|4\rangle + \Omega_a(t)|-4\rangle}{\sqrt{\Omega_a(t) + \Omega_b(t)}},$$

where $\Omega_a(t)$ and $\Omega_b(t)$ are time-dependent functions that vary adiabatically with time. We note that any arbitrary superposition of the two ground spin states $|4\rangle$ and $|-4\rangle$ can be prepared by appropriately...
tailoring the shapes of pulse of the transverse magnetic fields. That is, we can coherently control the spin states of molecular magnets by adiabatically changing the Rabi frequencies.

In order to clearly explain the process of coherent control of spin states, we take two special examples that are showed in Figures 2 and 3 respectively. In the case showed in Figure 2, the initial state is $|4\rangle$. In the beginning, the Rabi frequency $\Omega_b$ adiabatically increases from zero and $\Omega_a$ keeps zero. It easy to verify that the initial state is right the dark state at the moment. Because only the population of the spin state $|4\rangle$ is nonzero, the mixing angle $\theta$ is zero. After $\Omega_b$ increases to some value, we decrease $\Omega_b$ and increase $\Omega_a$ from zero adiabatically. When $\Omega_b$ vanishes, $\Omega_a$ arrives to a finite value. Simultaneously, the mixing angle $\theta$ changes from 0 to $\pi/2$, so the coherent population transfer is realized from $|4\rangle$ to $|-4\rangle$, i.e., one can coherently control the evolution of the spin state from $|4\rangle$ to $|-4\rangle$ by this scheme. In Figure 3, we show another case that the coherent and adiabatic evolution of the spin state from $|4\rangle$ to $1/\sqrt{2}(|4\rangle + |-4\rangle)$ is realized. In this case, firstly, we increase $\Omega_b$ to a finite value and $\Omega_a$ is zero as the previous case. Next, we keep $\Omega_b$ invariant and adiabatically increase $\Omega_a$ to the same value from zero. Finally, we decrease $\Omega_a$ and $\Omega_b$ to zero simultaneously. The last two steps are different from that of the previous case and the mixing angle varies from 0 to $\pi/4$. In the end, the populations of the spin states $|4\rangle$ and $|-4\rangle$ are both 1/2. From Figure 3 we can see that the coherent control of spin states from $|4\rangle$ to $1/\sqrt{2}(|4\rangle + |-4\rangle)$ is realized by our scheme.

![Diagram](image)

**FIG. 3:** The diagram of coherent control of spin states $|4\rangle \rightarrow 1/\sqrt{2}(|4\rangle + |-4\rangle)$. (a) the Rabi frequencies; (b) the mixing angle; (c) the population of spin states

Until now, we have not yet discussed the adiabatic condition for evolution of the dark state in this paper. In order to interpret adiabatic evolution of the dark state, we take the case shown in Figure 2 as example. In Figure 4, we draw the variation of eigenvalues of the three eigenstates with time in the condition shown in Figure 2. At the initial time, all the transverse magnetic fields are not added, $|4\rangle$ is just the dark state $|\Psi_0\rangle$ and the three eigenstates are degenerate. In interval I, $\Omega_b$ is added and $\Omega_a$ keeps zero, the energy gaps between the dark state and the other eigenstates appear but the eigenvalue of the dark state $|\Psi_0\rangle$ remains unchanged. During interval II, both $\Omega_a$ and $\Omega_b$ are nonzero, the dark state has $|4\rangle$ and $|-4\rangle$ components and the energy splitting of eigenvalues $E_{\pm}$ and
E_0 is largest. In interval III, the Rabi frequency Ω_b is zero and Ω_a gradually decreases to zero, the energy splitting of eigenenergies gradually disappears. From above we can see that there always exist gaps between eigenvalues E_± and E_0 in our operation time. In other cases besides the example, the processes are similar. Thus, if we choose the spin state |4⟩, which is right the dark state in interval I, as the initial state, it is possible to evolve adiabatically the dark state to our requested quantum state by adding special transverse magnetic field pulses.

In order to realize adiabatic evolution of the dark state, it is necessary that the amplitudes of transverse magnetic fields are large enough. If the coupling is insufficient, i.e. the Rabi frequencies are too small, the practical quantum state can not follow the evolution of the dark state due to nonadiabatic transfer to the states |Ψ±⟩ and |Ψ−⟩ may occur. The Hamiltonian matrix element for nonadiabatic coupling between the state |Ψ_0⟩ and the states |Ψ±⟩ or |Ψ−⟩ is given by ⟨Ψ±|Ψ_0⟩. Thus, the adiabatic condition is

\[
\left| \langle \Psi_\pm | \Psi_0 \rangle \right| \ll \frac{|E_\pm - E_0|}{\hbar},
\]

(16)

When the transverse magnetic field pulses have a smooth shape, a convenient adiabaticity criterion may be derived from Eq. (16) by taking a time average of the left-hand side, \( \langle \Psi_\pm | \Psi_0 \rangle_{av} = \pi/2\Delta \tau \), where \( \Delta \tau \) is the period during which the pulses overlap. This average value should not exceed the right-side, \( |E_\pm - E_0|/\hbar = \sqrt{\Omega_a^2 + \Omega_b^2}/2 \). The adiabatic condition is

\[
\Omega_{av}\Delta \tau > 10
\]

(17)

where \( \Omega_{av} \) is the average Rabi frequency of \( \Omega_a \) and \( \Omega_b \), and the number 10 is obtained from experience and numerical simulation studies.

The experimental work [11] shows that, in Ni_4 molecules, the longitudinal relaxation time is long, and its order is ~ s. Here we assume that \( \Delta \tau \) has the same order with the relaxation time. From this relaxation time and Eq. (17), we obtain the restriction for the average Rabi frequencies is \( \Omega_{av} > 10^\text{s}^{-1} \). In our scheme, it is proper that we choose the detuning \( \Delta \) as 1GHz. Thus, from Eq. (10) or (11), we know that \( \Omega_i > 2.6 \times 10^7 \text{s}^{-1} \), where \( \Omega_i = g\mu_B B_i/\hbar \) is the average value of \( \Omega_i = g\mu_B B_i/\hbar \). Here we introduce the average transverse magnetic field \( B_i \). Reference [10] shows \( g \sim 2.2 \). Finally we obtain the amplitude of the transverse magnetic fields required in our scheme as \( B_i > 8.4 \times 10^{-4} \text{T} \). In our scheme, the precise matching between the sum of frequencies of the left circularly polarized transverse magnetic fields \( \sum_{i=1}^{3} \nu_i \) and the sum of frequencies of the right circularly polarized transverse magnetic fields \( \sum_{i=4}^{7} \nu_i \) is required, but a finite detuning between \( \sum_{i=1}^{3} \nu_i \) and the gap of the spin states |0⟩ and |4⟩, \( \omega_0 - \omega_4 \), or between \( \sum_{i=4}^{7} \nu_i \) and the gap of the spin states |0⟩ and |−4⟩, \( \omega_0 - \omega_{−4} \), does not prevent the dark resonance. From the above estimation, we can see that the conditions required in our scheme are accessible experimentally.

**FIG. 4:** The variation of eigenvalues of the three eigenstates of the Hamiltonian with time in the condition presented in Figure 2.
In conclusion, using the method suggested by us, one can prepare any arbitrary superposition of the spin states $|4\rangle$ and $|-4\rangle$ from the ground spin state $|4\rangle$ or $|-4\rangle$. In molecular magnets, there is a potential barrier between the spin states with positive magnetic numbers and with negative ones, as is shown in Figure 1. In the absence of longitudinal magnetic field, each molecule has a double, Kramers degeneracy in its ground states. In Ni$_4$ molecules, they are $|4\rangle$ and $|-4\rangle$. The transition from one ground state to the other is possible only if the molecule jumps over the potential barrier or tunnels through it. Moreover, it is difficult to coherently control the transition caused by jumping over or tunnelling through the potential barrier and these schemes are not spin-state-selective. However, our scheme is spin-state-selective and the process is coherent. Therefore, Through adjustment of the magnitudes of the transverse magnetic fields, any arbitrary superposition of the two spin states of Ni$_4$ molecule can be obtained, i.e., the coherent control of spin states in molecular magnet, Ni$_4$, is realized.

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