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Famous for the Heisenberg uncertainty principle, Werner Heisenberg contributed hugely to the development of quantum mechanics, especially with his work on the matrix formulation. He also led important progress in fluid dynamics, quantum field theory, cosmic rays, and ferromgnetism. In his paper *On the Theory of Ferromagnetism*, Werner Heisenberg identifies the electrostatic interaction between electrons as the basis for ferromagnetic order for the first time. The "exchange integral" he discussed not only suggests preliminary explanation for the conditions of ferromagnetism, but also leads to new topics that are actively studied till present time.

Background Motivation

With the understanding of electromagnetism and atomic theory, study on magnetism begun at 19th century. Even though diamagnetism and paramagnetism were explained with Lorentz force and dipole moment of orbiting electrons respectively, people could not find a classical theory for ferromagnetism. Experiments show that there exists critical temperature for ferromagnets: below T_c, the material has a spontaneous magnetization even without external field, which shows its ferromagnetic ordering; above T_c, the ordering is destroyed by thermal fluctuations, and the material behaves paramagnetically. Within the paramagnetic regime, ferromagnets are found to obey the Curie-Weiss law:

$$\chi = \frac{C}{T - T_c},$$

which can be distinguished from a normal paramagnet oberying Curie law[5]:

$$\chi = \frac{C}{T}.$$

In 1907, Pierre Weiss proposed Mean Molecular Field Theory, which assumes an internal magnetic field proportional to the magnetization (M), so by calculations[4]:

$$M = N\mu \tanh\left(\frac{\mu(H_{ext} + \lambda M)}{k_B T}\right).$$

Hence when there's no external field, there is still a non-zero solution for M, which demonstrates the spontaneous magnetization of ferromagnet. Moreover, calculating susceptibility for high temperature with

$$\chi = \frac{\partial M}{\partial H},$$

one obtains the Curie-Weiss law. Though the theory explains the ferromagnetic behavior well, the origin of the "internal magnetic field" remained a problem. Naturally, one might think about the net magnetization as phenomenon due to magnetic interactions. Yet according to experiments, the internal field must be a few orders of magnitude larger than the possible resultant fields from magnetic interactions between atoms. On the other hand, the electrical interactions between atoms does not fall off with distance as Weiss's theory suggests[1].

Meanwhile, Samuel Goudsmit and George Uhlenbeck discovered the intrinsic magnetic moment of spinning electrons, and Einstein-de-Haas effect showed that the gyromagnetic ratio for electrons is roughly 2. With these established studies, Heisenberg identified that the orientation of magnetic moments of spinning electrons are in fact responsible for the magnetization, instead of those of atoms[4]. Connecting to his own research on many-electron system at that time, he pointed out that the strong coupling of the orientation stems from the quantum-mechanical exchange phenomenon.

Heitler-London Approximation

In his paper, Heisenberg refers to 3 approximation methods to calculate the energies: Pauli-Sommerfeld free electron model, Bloch tight-binding model, and London-Heitler theory[1]. The first model treats electrons as free and adds interactions with the lattice as perturbation, and the second approximates the background as a periodic potential and adds coupling between different Brillouin zones as perturbation. Only the London-Heitler theory, formulated in 1927 to explain the He spectrum, takes the interactions between electrons into account, and Heisenberg generalizes its exchange expression to explain the ferromagnetic phase in 2n-electron system.

If electron-electron interaction is ignored, the solution to a two-electron problem can be constructed from independent electron approximation: namely, the overall orbital wavefunction is a linear combination of product states of one-electron solutions. Say the eigenfunctions with two lowest energies to the Schrodinger equation

$$H\psi = E\psi, H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{|r - R_K|} + \frac{e^2}{|r - R_\lambda|}$$

are $\psi_0(r), \psi_1(r)$, then the lowest symmetric and antisymmetric overall orbital wavefunctions are given by

$$\Psi_{sym} = \psi_0(r_1)\psi_0(r_2), \Psi_{anti} = \psi_0(r_1)\psi_1(r_2) - \psi_1(r_1)\psi_0(r_2).$$

The one-electron problem was solved to give bonding and anti-bonding wavefunctions:

$$\psi_0(r) = \phi_K(r) + \phi_\lambda(r), \psi_1(r) = \phi_K(r) - \phi_\lambda(r)$$

, before normalization, where ϕ_μ is the atomic orbital around nucleus at μ. Plugging in gives the orbital wavefunctions as[5]

$$\Psi_{sym} = \phi_K(r_1)\phi_\lambda(r_2) + \phi_\lambda(r_1)\phi_K(r_2) + \phi_\lambda(r_1)\phi_\lambda(r_2) + \phi_K(r_1)\phi_K(r_2)\,,$$

$$\Psi_{anti} = 2(\phi_\lambda(r_1)\phi_K(r_2) - \phi_K(r_1)\phi_K(r_2))\,.$$

However, the symmetric orbital given by independent electron approximation would lead to an energy too high if electron-electron interaction is considered. The first two terms (which Heisenberg refers to as "simple transpositions") describe the case of each atom surrounded closely by one electron, while the last two terms describe two electrons around a single atom, leaving the other atom empty. Hence, the latter scenario leads to high interaction energy due to e-e repulsion. A modified wavefunction would give much lower energy:

$$\Psi_{sym} = \phi_K(r_1)\phi_K(r_2) + \phi_K(r_1)\phi_\lambda(r_2)\,,$$

which is referred to as Heitler-London approximation[5]. Since the case of two electrons being close together is excluded, this approximation works better when the nuclei are separated relatively far in the material and the wavefunctions of electrons are localized.

Exchange Integral and Ferromagnetism

The addition of two spin-1/2 particles gives either antisymmetric singlet state (when two quantum spins are antiparallel) or symmetric triplet state (when two spins are parallel). Pauli exclusion principle requires the overall wavefunction of fermions to be antisymmetric, so the symmetric orbital function is tensored with antisymmetric spin function, and the antisymmetric orbital with symmetric spin. Due to this determined pairing of orbital and spin, the energy difference between the two orbital wavefunctions can be regarded as the resultant energy splitting between singlet and triplets states:

$$E_s - E_t = \frac{<\Psi_{sym}|H|\Psi_{sym}>}{<\Psi_{sym}|\Psi_{sym}>} - \frac{<\Psi_{anti}|H|\Psi_{anti}>}{<\Psi_{anti}|\Psi_{anti}>}\,.$$

Since the splitting is caused by the quantum-mechanical exchange phenomenon, it is also called "exchange integral" J (with a factor of 2). Plugging in the wavefunctions and taking the limit of large spatial separation gives[5]:

$$J = \frac{E_s\text{-}E_t}{2} = \int dr_1 dr_2 (\phi_K(r_1)\phi_\lambda(r_2)) \left(\frac{e^2}{|r_1\text{-}r_2|} + \frac{e^2}{|R_K\text{-}R_\lambda|} - \frac{e^2}{|r_1\text{-}R_K|} - \frac{e^2}{|r_2\text{-}R_\lambda|} \right) (\phi_\lambda(r_1)\phi_K(r_2))\,.$$

Hence, the sign of the exchange integral tells which overall spin state is favored.

Recognizing the similarity between the singlet/triplet perference and the ferromagnetic ordering, Heisenberg generalizes the Heitler-London method to 2n-electron system and successfully demonstrates that the exchange term "generates" the Weiss molecular field. Because the terms in J are due to electrostatic interaction, the integral gives

the correct order of magnitude to account for the ad hoc Weiss field. Heisenberg uses the following notation in his paper to express the generalized exchange integral[1]:

$$J_{kl} = \frac{1}{2} \int d\tau_k d\tau_l \psi_k^K \psi_k^\lambda \psi_l^K \psi_l^\lambda \left(\frac{2e^2}{r_{kl}} + \frac{2e^2}{r_{K\lambda}} - \frac{e^2}{r_{Kk}} - \frac{e^2}{r_{Kl}} - \frac{e^2}{r_{\lambda k}} - \frac{e^2}{r_{\lambda l}} \right),$$

where k and l are the electrons, K and λ are atoms, and the factors of 2 come from summing each interaction pairs twice. Because of the first recognition of exchange interaction as the explanation for orderings in spins, and the explicit expression for J in many-electron system, the spin-dependent part of Hamiltonian

$$H = -\sum J_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

is referred to as Heisenberg model even though it is not in the original paper[4].

To evaluate the magnetization, Heisenberg makes the assumption that the energies for a given total spin s of the system follows Gaussian distribution[1]. He then calculates the mean and variance of the energies:

$$E_\sigma = \frac{1}{f_\sigma} \sum_P \chi_\sigma^P J_P , \quad \overline{\Delta E_\sigma^2} = \frac{1}{f_\sigma^2} \sum_{P,P'} (\chi_\sigma^E \chi_\sigma^{P,P'} - \chi_\sigma^P \chi_\sigma^{P,P'}) J_P J_{P,P'} ,$$

where σ is the set of energy levels with total spin s, χ_σ^P is the group character of permutation P, and $f_\sigma = \chi_\sigma^E$ is the number of levels. With only nearest neighbor terms and setting all J_P equal as some J_0, he then gets the result:

$$E_\sigma = -z \frac{s^2+n^2}{2n} J_0 + J_E , \quad \overline{\Delta E_\sigma^2} = J_0{}^2 z \frac{(n^2-s^2)(3n^3-s^2)}{4n^3} ,$$

where z is the number of nearest neighbor, and J_E is the Coulomb interactions between 2 electrons, 2 atoms, and electrons and atoms[1]. With the distribution, Heisenberg then calculates the partition function S by summing up all possible total spin cases (–n to n), and finds the expected value of magnetization m:

$$m_0 = \frac{\partial \ln S}{\partial \alpha} = n \tan \frac{\alpha + \beta \frac{m_0}{n} - \beta^2 \frac{m_0}{nz} + \beta^2 \frac{m_0{}^3}{2n^3 z}}{2} ,$$

with definitions[1]

$$\alpha = \frac{\hbar e}{m_e c} \frac{1}{k_B T} H , \quad \beta = \frac{z J_0}{k_B T} .$$

Showing that the formula for m only differs from Weiss's formula in a term cubic in $\frac{m_0}{n}$ (so can be neglected for large n), Heisenberg succeeds in reproducing the Weiss molecular field with the exchange interaction. The only concern in the process is the seemingly arbitrary assumption of Gaussian distribution. In fact, Heisenberg himself notes in his paper that it gives rise to a nonphysical result at low temperature. For the equation to have a nonzero solution, the condition for ferromagnetic is expressed as[1]:

$$\beta \left(1 - \frac{\beta}{z}\right) \geq 2 \ .$$

Because the peak of the left hand side is achieved at $\beta = \frac{z}{2}$, it then leads to the result that $z \geq$ 8 for ferromagnetism to take place. Another important criterion is J_0 being positive, which Heisenberg does not give a definite answer to. But arguing high quantum principle number n results in positive J_0, Heisenberg puts a rough boundary at n = $3^{[1]}$.

Antiferromagnetism and Quantum Spin Liquid

While Heisenberg model with positive J explains the existence of ferromagnetism, negative J leads to other numerous interesting topics: J < 0 implies the antiferromagnetic case, where quantum spins are favored to align antiparallel. Different antiferromagnetic interactions can conflict with each other, and when the lattice structure doesn't allow them to be simultaneously satisfied, the material is said to be frustrated[3]. The simplest example might be an Ising antiferromagnet on a triangular lattice with equal nearest neighbor interactions has geometric frustration: if two spins on a triangle are set to align antiparallel, the last one cannot satisfy the preferred interactions with both neighbors at the same time. Existence of frustration is connected to an exotic phase: quantum spin liquid (QSL).

In 1973, P.W.Anderson first proposed the term in his paper. He used it to describe a special state called resonance valence bond (RVB), and claimed that it is the ground state of Heisenberg antiferromagnet on a triangular lattice, which was proven to be incorrect[2]. "Liquid" refers to the disorderness of the system, and spin liquid is a system of spins with high entanglement yet without an ordering. A spin liquid can be classical or quantum, where classical spin liquid is disordered due to thermal fluctuations and a high degeneracy of states to transfer between, and a QSL is due to quantum fluctuation. Hence despite their spins are highly correlated, a classical spin liquid can retain disorderness down to very low temperature, and a QSL can be disordered even at absolute zero. Typically, frustration leads to necessary compromise of one of the competing exchange interactions, and the choice of which bond to compromise can give a high degeneracy, so frustration is often a defining feature of QSL. In 1987, Anderson and others proposed that doping a QSL can give rise to superconductivity. Around 2000, people noticed the use of QSL in quantum computation due to its robustness in error[2]. Furthermore, studying QSL is also related to Majorana particles, magnetic monopoles, and topological orders, etc. The richness of possibilities in QSL stirs constant hot debate around it till nowadays.

Usually QSL is identified as the lack of magnetic order at zero temperature, but a positive definition makes it easier to work with. In that context, QSL is often identified as

phase with extremely high entanglement, which means it can't be smoothly deformed into a finite product state[2]. Even then, it is hard to measure the degree of entanglement, so the experimental realization of QSL has been challenging. Yet, there already exist theoretically contrived models that help people understand general properties of QSL and provide references for experimental work.

Theoretical Model of QSL

One of the earliest models is toric code model proposed by Alexei Kitaev in 1997, which is similar to Heisenberg model, but "entangles" 4 spins at a time. It is a model (originally) defined on a 2D square lattice with periodic boundary condition, spins at the middle of each edge of the squares, and a Hamiltonian:

$$H = -J \sum_p P_p - J' \sum_s S_s$$

, where the operator first term is summed over all plaquettes on the lattice and the second term is summed over all sites (as shown by blue and red lines in the Fig.1), and "plaquette" and "star" operators are tensors of Pauli spin matrices[2]:

$$P_p = \prod_{i \in p} \sigma_i^z , S_s = \prod_{i \in s} \sigma_i^x .$$

Taking one plaquette and one star operator, they either not overlap or overlap on two edges. Because one action of σ_i^x flips z-based eigenstates once and the eigenvalues for σ_i^z are ± 1, two overlapping edges mean the measured eigenvalues are flipped twice: $(-1)^2 = 1$. Thence, the action of S_s would not change the result of P_p, and the same applies for vice versa; namely, S_s and P_p commute. Consequently, minimizing the energy to find the ground state is the same as maximizing the eigenvalue of each $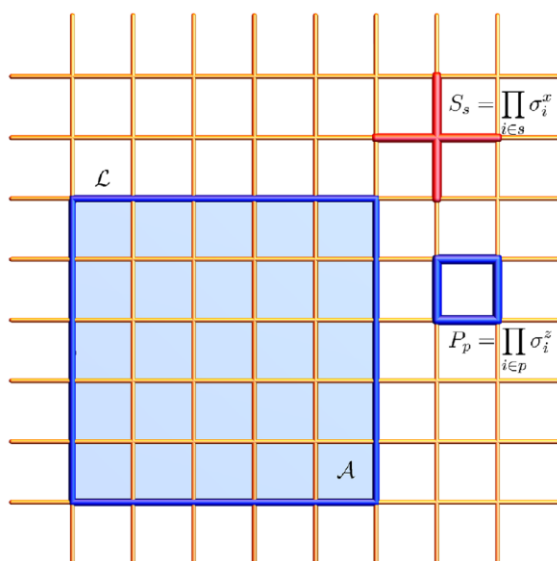S_s$ and P_p operator at the same time, so the ground state occurs when each individual operator gives +1. Obviously, this is a highly-entangled phase: for a star to give +1, there must be an even number of spins corresponding

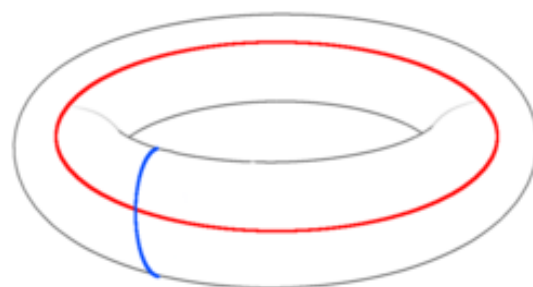Fig. 1 Operators of the toric code model[2]

Fig. 2 Periodic boundary condition of the toric code model

to eigenvalues -1, so measuring some of the 4 spins gives information on the rest, and this applies to every single site and plaquette.

Degeneracy is also found in this model. Consider the loop operator L as a larger version of P_p, only that now the spins acted on are only those on the contour L. Then a trivial L can be regarded as the multiplying all the plaquettes inside together, since all the interior edges are multiplied twice and give +1. Then for ground state, because each small P_p needs to be +1, any L that can be expressed as tensor of P_p should also give +1. However, there are two non-trivial loops: the ones going around the torus (the shape is due to the periodic boundary condition), as shown in Fig.2. If a strip of plaquesttes are multiplied together, the resultant contour would be two parallel loops. This gives 4-fold degeneracy for ground state, since each of the non-trivial loop can then be either +1 or -1.

Other general features of QSL that the toric code model demonstrates are non-local excitation and anyon statistics. The minimal excitation to the ground state is taking one S_s or P_p to be -1, so that the total energy is raised by 2J or 2J' respectively. Exciting an individual star or plaquette is referred to as electric (e) or magnetic (m) particles, so e sits on lattice sites and m sits in the middle of lattice sites[2]. Locally, e and m particles can only be created in pairs since any action on a single edge/spin, such as acting σ_i^z on one spin, always involves two plaquettes and two stars. To create an isolated particle, it is necessary to take a non-local excitation. For example, action of a line of σ_i^z only flips the stars at the end of the line (the stars in the middle are unchanged because of an even number of flipping), hence creating 2 m particles separated from each other. The non-locality leads to the exotic mutual statistics between e and m[2]. Considering there exist an isolated m and an isolated e particles, which represents the state of the system with one star and one plaquette being -1, the rest all +1. Again because σ_i^z flips x-based eigenstates, acting σ_i^z on an edge can be regarded as translating the e particle. If the e particle is move along a closed loop around m, the action is equivalent to take the loop operator L on the initial state, which is the same as the product of all plaquettes inside as mentioned before. Yet due to the existence of an m particle in the middle, there is one plaquette with value -1, so the overall effect is multiply by -1 and the final state is off by a π phase shift[2].

There are also other theoretical models proposed for QSL ground state, including the honeycomb, Heisenberg model on other lattices, etc. They are usually contrived quite artificially and share similar features discussed above.

Experimental Realization of QSL

Because most properties of QSL are hard to measure, like entanglement and non-locality, there are few experimental signatures that can be used to identify QSL. The widely-accepted defining feature – lack of magnetic order at zero temperature – is not easy to verify neither. Typically, identification requires combining multiple measurements together for analysis, or perfect match with some theoretical models. So far, there is still no clear evidence for any experimental realization. Practically, frustration is an important aspect that people examine when looking for QSL; it can be caused either by next nearest neighbor interaction or just geometry of the lattice[2]. Commonly used techniques include NMR and muon spin resonance to measure magnetic ordering, neutron scattering to probe excitations, and specific heat measurements to match with theoretical models. Though there exist some candidates, such as herbersmithite and triangular organics, none has a perfect matching with theoretical models[2][3].

Summary

Correctly identifying the electrostatic interactions between electrons as the origin for the Weiss molecular field, Heisenberg demonstrates the significance of electron-electron interaction and provides the basis for explaining the ferromagnetism. His calculations on the exchange phenomenon match the experimental observations and set the first conditions on ferromagnetism. Furthermore, the Heisenberg model generated by his exchange integral inspires other profound discussions. Particularly, the antiferromagnetic interactions leads to the topic of quantum spin liquid, which is intensely studied on till today.

Reference:

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