

Heisenberg and Ferromagnetism

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Heisenberg's contributions to the understanding of ferromagnetism are reviewed. The special features of ferromagnetism, vis-a-vis dia and paramagnetism, are introduced and the necessity of a Weiss molecular field is explained. It is shown how Heisenberg identified the quantum mechanical exchange interaction, which first appeared in the context of chemical bonding, to be the essential agency, contributing to the co-operative ordering process in ferromagnetism.

Though magnetism was known to the Chinese way back in 2500 BC, and to the Greeks since 600 BC, it was only in the 19th century that systematic quantitative studies on magnetism were undertaken, notably by Faraday, Guoy and Pierre Curie. Magnetic materials were then classified as dia, para and ferromagnetics. Theoretical understanding of these phenomena required inputs from two sources, (1) electromagnetism and (2) atomic theory. Electromagnetism, that unified electricity and magnetism, showed that moving charges produce magnetic fields and moving magnets produce emfs in conductors. The fact that electrons (discovered in 1897) reside in atoms directed attention to the question whether magnetic properties of materials had a relation with the motion of electrons in atoms.

The theory of diamagnetism was successfully explained to be due to the Lorentz force $\mathbf{F} = e[\mathbf{E} + (1/c)\mathbf{v} \times \mathbf{H}]$, on an orbiting electron when a magnetic field \mathbf{H} is applied. Here \mathbf{v} is the velocity of the electron and 'e' the electronic charge (Langevin 1905, Pauli 1920). This changes the electric current in the electron orbit, in a way that gives an induced magnetisation $M_{\text{induced}} =$



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$-(Ne^2/6mc^2)z\langle r^2\rangle\mathbf{H}$, where $\sqrt{\langle r^2\rangle}$ is the typical radius of the electron orbit in the atom, with the negative sign implying that the induced effect opposes the external applied one, 'N' is the number of atoms per unit volume and 'z' is the atomic number, i.e. the number of electrons per atom and 'm' is the electronic mass. Diamagnetism is a universal phenomenon present in all substances, but being a feeble effect, may be subsumed by paramagnetism if paramagnetism is present. Paramagnetism of materials, as was rightly concluded, is related to the fact that atoms or molecules can have permanent dipole moments. These permanent dipole moments arise due to the fact that every orbiting electron is a current loop, that acts as a tiny magnetic shell, giving by Ampere's law, a magnetic moment

$$\vec{\mu} = \mu_B \Sigma(\mathbf{L}_i + 2\mathbf{S}_i). \quad (1)$$

Here, $\mu_B = (eh/4\pi mc)$ is called the Bohr magneton, \mathbf{L}_i and \mathbf{S}_i are the quantum numbers of orbital and spin angular momenta respectively, 'h' is the Planck constant and the summation in (1) is evaluated for all the 'z' electrons in the atom. Whether an atom or a molecule has a permanent dipole moment or not is decided by whether the sum in (1) is non zero or not – a scheme that is documented in several text books.

Physicists, however, failed to understand ferromagnetism from an atomic basis. It was Heisenberg's work in the late 1920's that filled this void. To accomplish this, quantum mechanics had to be discovered first. This was done mainly to understand atomic spectra. It was indeed in the fitness of things that the quantum dynamics of the electron left an imprint on another area, namely magnetism, which too had to do with the magnetic effects of electron dynamics. To understand this development we take a little digression into the phenomenology of ferromagnetism and into the area of electron bonding, which to most of the classical physicists were



unconnected phenomena. It was Heisenberg, who saw the connection and established it in two seminal papers, written in 1926 and 1928.

Ferromagnetism

It was found that certain substances like iron, cobalt, nickel, etc., when cooled below a certain temperature T_c (called the critical temperature) developed a spontaneous magnetization, even in the absence of an external magnetic field. The temperature variation of the magnetic susceptibility above the critical temperature was found to follow the Curie–Weiss law $\chi_{\text{ferro}} = C/(T - T_c)$, whereas an ordinary paramagnet shows the Curie law: $\chi = C/T$. It was Weiss, in 1907, who correctly understood that this dependence was due to an internal magnetic field \mathbf{H}_{int} , called the molecular magnetic field. This was such that if an external magnetic field \mathbf{H} is applied, then every atom in the substance finds itself in an effective magnetic field

$$\mathbf{H}_{\text{eff}} = \mathbf{H} + \mathbf{H}_{\text{int}} = \mathbf{H} + \alpha \mathbf{M}. \quad (2)$$

Here \mathbf{M} , the magnetization, is given by

$$\mathbf{M} = \sum \mu_j, \quad (3)$$

where the summation is over all atoms, present in a unit volume and $\alpha > 0$, is a parameter characteristic of the substance. This internal field $\mathbf{H}_{\text{int}} = \alpha \mathbf{M}$ is seen to play an ordering effect as can be seen below. If we bring a dipole from outside and place it in the internal field, the dipole will be aligned in the direction of this internal field, i.e., in the direction of the magnetization itself, giving rise to a spontaneous ordering, i.e., yield a ferromagnetic state. This ordering effect is indeed destroyed by the randomizing energy $k_B T$ arising due to thermal effects, trying to flip the dipole away from this ordered state. Calculations of the magnetization show that (if the dipoles can align only in two directions \uparrow and \downarrow),

$$M(H) = N\mu \tanh(\mu[H + \alpha M]/k_B T). \quad (4)$$

The question was this: If every atom has an outer cloud of electrons, then how do atoms approach each other to form a chemical bond? It was Heisenberg who showed that the interaction between electrons, called the exchange energy was the basis of the Weiss molecular field.

In the absence of the external magnetic field ($H = 0$), the magnetization follows

$$M = N\mu \tanh(\mu\alpha M/k_B T). \quad (5)$$

This shows that a non zero solution for M i.e. a spontaneous magnetization is possible only if $T < T_c = N\mu^2\alpha/k_B$. The susceptibility is seen to follow, for high temperatures,

$$\chi_{\text{ferro}} \equiv \partial M(H)/\partial H \approx (N\mu^2/k_B)/(T - T_c) \quad (6)$$

obeying the experimentally observed Curie–Weiss law, while the spontaneous magnetization follows

$M(H = 0, T) \propto \sqrt{(T_c - T)}$, for $T \leq T_c$. From the fact that the transition temperature T_c follows $k_B T_c = N\mu^2\alpha$, it is clear that the ordered ferromagnetic state can occur when the diminution of energy, $N\mu^2\alpha$, per dipole, due to ferromagnetic ordering exceeds the randomizing thermal energy $k_B T$.

The question that still remained unanswered was this: what is the origin of this ordering field $\mathbf{H}_{\text{int}} = \alpha\mathbf{M}$, that gives rise to a co-operative phenomenon below T_c ?

Chemical Bonds

The dynamics of scientific progress is indeed one of co-operative phenomenon, where the seeds of the breakthrough in one field may be sown in another. So was the case with magnetism, where the fundamental mechanism for the origin of the co-operative field was being investigated in the field of spectroscopy, in trying to understand the origin of the chemical bond. The chemist had a dilemma ever since the discovery of the electron. The question was this: if every atom has an outer cloud of electrons, then how do atoms approach each other to form a chemical bond? The problem was first tried by Pauli (1926) in the context of the helium atom and by Heitler and London (1927) for the hydrogen molecule.



The above works can be classified under spectroscopy and chemical bonding but it was Heisenberg who showed that the interaction between electrons, called the exchange energy was indeed the basis of the Weiss molecular field. It is here that some experimental results are in order. In most cases it is seen that: $k_B T_c \approx 10^{-14}$ erg. The dipole-dipole interaction between the atomic dipoles, kept at about 1 Angstrom (10^{-8} cm) away can contribute only an energy of the order of 10^{-16} ergs, hence a stronger agency is required to bring in the Weiss molecular field. Heisenberg correctly identified that the exchange energy, which is of electrostatic origin (with a typical energy 10^{-14} erg and *not* a dipole-dipole interaction) and is purely quantum mechanical in nature, lies at the core of what gives rise to the Weiss field.

According to the Heitler-London theory, if there are two atoms, '1' and '2' each having a single electron, one can assume them to be in atomic states 'j' and 'k' the orbital wave functions for this two-electron system can be constructed from the linear combinations of the quantities $\psi_j(\mathbf{r}_1)\psi_k(\mathbf{r}_2)$, $\psi_j(\mathbf{r}_2)\psi_k(\mathbf{r}_1)$, where $\mathbf{r}_1, \mathbf{r}_2$ are the locations in space for the two electrons. The possible wave functions are

$$\psi_+(\mathbf{r}_1\mathbf{r}_2) = \psi_j(\mathbf{r}_1)\psi_k(\mathbf{r}_2) + \psi_j(\mathbf{r}_2)\psi_k(\mathbf{r}_1), \quad (7)$$

$$\psi_-(\mathbf{r}_1\mathbf{r}_2) = \psi_j(\mathbf{r}_1)\psi_k(\mathbf{r}_2) - \psi_j(\mathbf{r}_2)\psi_k(\mathbf{r}_1). \quad (8)$$

One must, in addition, consider the spin part of the wave function. The spin of any electron can point up \uparrow or down \downarrow . The spin part of the two electron wave function can be

$$S_1 = S(1, \uparrow)S(2, \uparrow) + S(1, \downarrow)S(2, \downarrow) \quad (9)$$

$$S_0 = S(1, \uparrow)S(2, \downarrow) - S(1, \downarrow)S(2, \uparrow). \quad (10)$$

In the case S_1 , since both the spins are pointing in the same direction, the net spin is ($s = 1/2 + 1/2 = 1$)

The total wave function of the two-electron system must combine both the orbital as well as the spin wave functions, and by the Pauli exclusion principle, should be such that if the two electrons are in the same state, the wave function must vanish identically.

while in the case S_0 , since the two spins are pointing in opposite directions, the net spin is ($s = 1/2 - 1/2 = 0$). The total number of possible states $g = 2s + 1$ gives the degeneracy of the respective states to be $g_0 = 1$ and $g_1 = 3$. Suppose we apply the external magnetic field in the z -direction, then for S_0 the z components of the spin can be $s_z = 0$, while for S_1 they can be $s_z = 1, 0, -1$.

The total wave function of the two-electron system must combine both the orbital as well as the spin wave functions, and by the Pauli exclusion principle, should be such that if the two electrons are in the same state, the wave function must vanish identically. It is seen that this is possible only if the wave functions are:

$$\psi_1(\mathbf{r}_1\mathbf{r}_2) = \psi_-(\mathbf{r}_1\mathbf{r}_2)S_1 \quad (11)$$

$$\psi_0(\mathbf{r}_1\mathbf{r}_2) = \psi_+(\mathbf{r}_1\mathbf{r}_2)S_0. \quad (12)$$

To find the energy eigenvalues of this two-electron system, one has to solve the Schrödinger equation

$$\{-(1/2m)(h/2\pi)^2[\nabla_1^2 + \nabla_2^2] + [V(\mathbf{r}_1) + V(\mathbf{r}_2)]\psi(\mathbf{r}_1, \mathbf{r}_2) + (e^2/|\mathbf{r}_1 - \mathbf{r}_2|)\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2), \quad (13)$$

where $\nabla_1^2 = \partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2$, $\nabla_2^2 = \partial^2/\partial x_2^2 + \partial^2/\partial y_2^2 + \partial^2/\partial z_2^2$, while $V(\mathbf{r}_1)$, $V(\mathbf{r}_2)$ are the potentials in the two atoms and the last term in the RHS of (10) describes the electrostatic Coulomb interaction between the two electrons. The atomic states ' j ' and ' k ' being those in the absence of the electron-electron Coulomb interaction, we have

$$\{-(1/2m)(h/2\pi)^2 \nabla_1^2 + V(\mathbf{r}_1)\}\psi_j(\mathbf{r}_1) = E_j\psi_j(\mathbf{r}_1) \quad (14)$$

$$\{-(1/2m)(h/2\pi)^2 \nabla_2^2 + V(\mathbf{r}_2)\}\psi_k(\mathbf{r}_2) = E_k\psi_k(\mathbf{r}_2). \quad (15)$$



Assuming the zeroth order wave functions to be $\psi_1(\mathbf{r}_1, \mathbf{r}_2)$, $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$, given in (11),(12), one finds in the first order approximation, the energy eigenvalues of the singlet (suffix 0) and the triplet (suffix 1) states to be

$$E_0 = (E_j + E_k) + C_{jk} + J_{jk} \quad (16)$$

$$E_1 = (E_j + E_k) + C_{jk} - J_{jk}. \quad (17)$$

Here the terms C_{jk} and J_{jk} are given by the integrals

$$C_{jk} = \int \int \psi_j^*(\mathbf{r}_1)\psi_k^*(\mathbf{r}_2)(e^2/|\mathbf{r}_1 - \mathbf{r}_2|)\psi_j(\mathbf{r}_1)\psi_k(\mathbf{r}_2)d^3\mathbf{r}_1d^3\mathbf{r}_2 \quad (18)$$

$$J_{jk} = \int \int \psi_j^*(\mathbf{r}_1)\psi_k^*(\mathbf{r}_2)(e^2/|\mathbf{r}_1 - \mathbf{r}_2|)\psi_k(\mathbf{r}_1)\psi_j(\mathbf{r}_2)d^3\mathbf{r}_1d^3\mathbf{r}_2. \quad (19)$$

It is seen that C_{jk} is the Coulomb energy of interaction between the two electrons, since $\psi_j^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1)$ gives the electron density at \mathbf{r}_1 , and $\psi_k^*(\mathbf{r}_2)\psi_k(\mathbf{r}_2)$ gives the electron density at \mathbf{r}_2 . The term J_{jk} is called the exchange integral (since $\psi_j^*(\mathbf{r}_1)$ couples with $\psi_k(\mathbf{r}_1)$ while $\psi_k^*(\mathbf{r}_2)$ couples with $\psi_j(\mathbf{r}_2)$) and has no classical analogue.

Exchange Interaction and Magnetism

Heisenberg's masterly contribution in magnetism lies in identifying this exchange term J_{jk} , which first appeared in the context of chemical bonding and spectroscopy, to be of central importance in explaining ferromagnetism. Heisenberg began in 1926 to explore how the exchange term appeared in a system of atoms with many electrons. In order to calculate the effect, he used the many-electron wave function to be a Slater determinant, so that the wave function is antisymmetric, thus making sure that no two electrons in the system can be in identical quantum states. He identified that the exchange term does appear and in a subsequent paper



Heisenberg's masterly contribution in magnetism lies in identifying the quantum mechanical exchange energy, first appearing in the context of chemical bonding and spectroscopy, to be of central importance in explaining ferromagnetism.

in 1928, Heisenberg proceeded to calculate by the well-known methods of statistical physics, the magnetization of such a system. The temperature dependence of magnetization was seen to follow that given in equation (4), if $J_{jk} > 0$, which led Heisenberg to conclude that the exchange interaction was the microscopic phenomenon that was central to the explanation of the Weiss molecular field. This can be seen from the fact that for $J_{jk} > 0$, the triplet state has a lower energy. This state, in which the two spins are aligned in the same direction is thus energetically favourable, helping in the ordering of the spins in a certain direction, as is seen in the ferromagnetic state.

The Heisenberg Hamiltonian and After

Modern theories of magnetism extensively use a Hamiltonian called the 'Heisenberg exchange Hamiltonian' to investigate the magnetic properties of materials. The Hamiltonian was, however, not introduced by Heisenberg, but by Dirac (1928). In this classic paper, Dirac showed that if there are two atoms located at points \mathbf{R}_1 and \mathbf{R}_2 , then the exchange interaction between the electrons in the two atoms can be obtained by just adding a term

$$H_{\text{exchange}} = -J(|\mathbf{R}_1 - \mathbf{R}_2|)[(1/2) + 2\mathbf{S}_1 \cdot \mathbf{S}_2], \quad (20)$$

where

$$J(|\mathbf{R}_1 - \mathbf{R}_2|) = \int \int \psi_j^*(|\mathbf{R}_1 - \mathbf{r}_1|) \psi_k^*(|\mathbf{R}_2 - \mathbf{r}_2|)$$

$$(e^2/|\mathbf{r}_1 - \mathbf{r}_2|) \psi_k(|\mathbf{R}_2 - \mathbf{r}_1|) \psi_j(|\mathbf{R}_1 - \mathbf{r}_2|) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \quad (21)$$

and $\mathbf{S}_1, \mathbf{S}_2$ are the spins of the two electrons present in the two atoms. The wave functions $\psi_j(|\mathbf{R}_1 - \mathbf{r}_1|)$ and $\psi_k(|\mathbf{R}_2 - \mathbf{r}_2|)$ are centered around atoms '1' and '2' respectively. In a system with many atoms located at different lattice sites \mathbf{R}_j , the total exchange energy must



involve all possible pairs of atoms present in the solid. The electron wave functions being highly localized (i.e. the function $\psi(\mathbf{r})$ falls off fast as the argument of the function increases), $J(|\mathbf{R}_1 - \mathbf{R}_2|)$ falls off rapidly for $|\mathbf{R}_1 - \mathbf{R}_2|$ larger than the typical atomic orbital radius. It thus suffices to include in the sum only the terms in which $\mathbf{R}_j, \mathbf{R}_k$ are the nearest neighbours, so that the spin dependent part of the exchange energy can be approximated as

$$H_{\text{exchange}} = -2\Sigma J(|\mathbf{R}_j - \mathbf{R}_k|)\mathbf{S}_j \cdot \mathbf{S}_k, \quad (22)$$

where the sites $\mathbf{R}_j, \mathbf{R}_k$ are the nearest neighbours in the lattice. Considering the typical nearest neighbour distance to be 'a' replacing \mathbf{S}_j by the average quantity $\mathbf{S}_j = \langle \mathbf{S}_j \rangle = \mathbf{S}$ and using the definition of magnetization to be $\mathbf{M} = (\mu_B N)\mathbf{S}$ and using $\mu_k = \mu_B \mathbf{S}_k$, we find the exchange energy to be $H_{\text{exchange}} = -(1/\mu_B^2 N)J(a)\Sigma \mathbf{M} \cdot \mu_k$ where the summation is over all the magnetic dipoles μ_k located at the different lattice sites \mathbf{R}_k , in the system. This expression for the exchange energy (called the mean field approximation) is then exactly the same as that for a system of dipoles μ_k placed in a magnetic field $\mathbf{H}_{\text{int}} = -(1/\mu_B^2 N)J(a)\mathbf{M}$, proportional to the magnetization \mathbf{M} , thus showing the origin of the Weiss molecular field (see equation (3)) to be due to the exchange interaction.

The richness of the Heisenberg Hamiltonian (22) was, however, not confined to the explanation to ferromagnetism, but opened the floodgates of new activities in the area of magnetism both in terms of thermodynamics and spin dynamics. Most notable amongst these that followed more or less immediately, were (1) the identification by Néel (1932) that the exchange integral J could be negative and could thus give rise to an antiferromagnetic ordering below a certain transition temperature, in which the nearest neighbours order themselves in such a way that their spins point in opposite directions; the concepts of (2) superexchange (Bitter 1938,

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Kramer 1941), (3) crystal field splitting (Van Vleck, 1932) and (4) domain structure and dynamics (Bloch 1932, Landau and Lifshitz 1935). Many of these phenomena, which have their origin in the Heisenberg exchange mechanism were found to be true, when neutron scattering techniques, developed in the post war era could allow the magnetic ordering to be observed at the microscopic scale.

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Suggested Reading

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“I think the greatest effort in the developments of theoretical physics is always necessary at those points where one has to abandon old concepts.”

“Almost every progress in science has been paid for by a sacrifice, for almost every new intellectual achievement previous positions and conceptions had to be given up. Thus, in a way, the increase of knowledge and insight diminishes continually the scientist’s claim on ‘understanding’ nature.”

“The history of physics is not only a sequence of experimental discoveries and observations, followed by their mathematical description; it is also a history of concepts.”

“In the experiments about atomic events we have to do with things and facts, with phenomena which are just as real as any phenomena in daily life. But the atoms or elementary particles are not as real: they form a world of potentialities or possibilities rather than one of things or facts.”

– *Werner Heisenberg*

