

LECTURE 17

Ferromagnetism

(Refs.: Sections 10.6-10.7 of Reif; Book by J. S. Smart, *Effective Field Theories of Magnetism*)

Consider a solid consisting of N identical atoms arranged in a regular lattice. Each atom has a net electronic spin \mathbf{S} and a magnetic moment $\vec{\mu}$ that is related to the spin by

$$\vec{\mu} = g\mu_o\mathbf{S} \quad (1)$$

where g is the g-factor and μ_o is the Bohr magneton. In the presence of an externally applied magnetic field H_o along the z direction, the Hamiltonian \mathcal{H}_o is given by

$$\mathcal{H}_o = -g\mu_o \sum_{j=1}^N \mathbf{S}_j \cdot \mathbf{H}_o = -g\mu_o H_o \sum_{j=1}^N S_{jz} \quad (2)$$

In addition, each atom can interact with its neighbors. In the past we ignored interactions and assumed that the spins were noninteracting. This is ok as long as $k_B T \gg$ the interaction energy. In this case, well-localized spins should obey Curie's law, $\chi \sim 1/T$, far from saturation and the magnetization M should vanish as $H_o \rightarrow 0$. This is how a paramagnet behaves.

However, if the interaction between spins $\gtrsim k_B T$, magnetic ordering may occur. We can think of this as being due to an effective magnetic field produced at a given site by its neighbors. For example, suppose a given electron is \uparrow . If it produces a field at a neighboring site parallel to itself, then the neighbor will also tend to be polarized \uparrow : in fact, we would expect all \uparrow spins or all \downarrow spins in the ground state. This is a *ferromagnet* – it has “spontaneous magnetization” even when $\mathbf{H}_o = 0$. Ferromagnets are bar magnets and stick to your refrigerator door. If, on the other hand, the field produced is antiparallel to the spin, we expect to get $\uparrow\downarrow\uparrow\downarrow \dots$. This is an *antiferromagnet* and has zero net magnetization.

All forms of magnetic ordering disappear as the substance is heated: typical transition temperatures are of order 100 to 1000 K. The temperature at which the spontaneous magnetization disappears is called the *Curie temperature* (T_C) for a ferromagnet. The ordering temperature for an antiferromagnet (AF) is called the Néel temperature (T_N).

Origin of the Ordering Field: Our first guess of the dominant magnetic interactions would be magnetic dipole-dipole interactions. But the strength of nearest neighbor dipole-dipole interactions is of order 1 K which is much smaller than the transition temperature (T_C) for a ferromagnet. (See Reif page 429 for more details of this estimate.) So dipolar interactions cannot account for magnetic ordering.

The origin of the ordering field is a quantum mechanical exchange effect. The derivation is given in the appendix and you will see it in the second quarter of quantum mechanics. Let me try to explain the physics behind the exchange effect. Basically the Coulomb interaction between two spins depends on whether the spins form a singlet

or a triplet. A triplet state is antisymmetric in real space while the singlet state has a symmetric wavefunction in real space. So the electrons stay out of each others way more when they are in the triplet state. As a result, the Coulomb interaction between two electrons is less when they are in a triplet state than when they are in a singlet state. So the interaction energy depends on the relative orientations of the spins. This can be generalized so the spins don't have to belong to electrons and the spins need not be spin-1/2. This interaction between spins is called the exchange interaction and the Hamiltonian can be written as

$$\mathcal{H} = -2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (3)$$

This is known as the Heisenberg Hamiltonian. We put $i > j$ in the sum to prevent double counting. J_{ij} is called an exchange constant. Since it depends on the overlap of wavefunctions, it falls off rapidly as the distance between the spins increases. Often J_{ij} is taken to be non-zero only between nearest neighbor spins. If we take $J_{ij} = J$, then

$$\mathcal{H} = -2J \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4)$$

Notice that if $J > 0$, then the spins lower their energy by aligning parallel to each other. If $J < 0$, the spins are anti-parallel in their lowest energy spin configuration. (In a spin glass, J_{ij} is a random number that is different for each pair i and j .)

The spins need not have $S = 1/2$. For example, if there is both spin and orbital angular momentum (\mathbf{S} and \mathbf{L}), then $\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i$ is the relevant "spin" vector. \mathbf{J}_i is the total angular momentum of the i th atom.

A simpler Hamiltonian can be obtained by just considering the z components of the spins. This is called the Ising model.

$$\mathcal{H} = -2J \sum_{i>j} S_{iz} S_{jz} \quad (5)$$

For $S = 1/2$, S_z can take only 2 values: $+1/2$ or $-1/2$.

Magnetic systems are not only important in their own right, but also because they are simple examples of interacting systems and can represent other types of systems, e.g., a system of neurons.

Weiss Mean Field (or Molecular Field) Theory of Ferromagnetism

This is a prototype for mean field theories and second order phase transitions. In 1907 Pierre Weiss proposed an effective field approximation in which he considered only one magnetic atom and replaced its interaction with the remainder of the crystal by an effective magnetic field \mathbf{H}_{eff} . We can extract the single atom Hamiltonian from the Heisenberg Hamiltonian:

$$\mathcal{H}_1 = -2\mathbf{S}_i \cdot \sum_j J_{ij} \mathbf{S}_j \quad (6)$$

We now wish to replace the interactions with other spins by an effective magnetic field \mathbf{H}_{eff} so that \mathcal{H}_1 has the form

$$\mathcal{H}_1 = -\vec{\mu}_i \cdot \mathbf{H}_{eff} = -g\mu_B \mathbf{S}_i \cdot \mathbf{H}_{eff} \quad (7)$$

where

$$\mathbf{H}_{eff} = \frac{2}{g\mu_B} \sum_j J_{ij} \mathbf{S}_j \quad (8)$$

In the spirit of the Weiss approximation, we then assume that each \mathbf{S}_j can be replaced by its average value $\langle \mathbf{S}_j \rangle = \langle \mathbf{S} \rangle$

$$\mathbf{H}_{eff} = \frac{2\langle \mathbf{S} \rangle}{g\mu_B} \left(\sum_j J_{ij} \right) \quad (9)$$

By assumption, all magnetic atoms are identical and equivalent. This implies that $\langle \mathbf{S} \rangle$ is related to the magnetization of the crystal by

$$\mathbf{M} = ng\mu_B \langle \mathbf{S} \rangle \quad (10)$$

where n is the number of spins per unit volume.

$$\begin{aligned} \mathbf{H}_{eff} &= \frac{2}{ng^2\mu_B^2} \left(\sum_j J_{ij} \right) \mathbf{M} \\ &= \lambda \mathbf{M} \end{aligned} \quad (11)$$

where λ is the Weiss molecular field coefficient:

$$\lambda = \frac{2}{ng^2\mu_B^2} \left(\sum_j J_{ij} \right) \quad (12)$$

If there are only nearest-neighbor interactions, $\sum_j J_{ij} = zJ$ where z is the number of nearest neighbors, i.e., the coordination number. Then

$$\lambda = \frac{2zJ}{ng^2\mu_B^2} \quad (13)$$

If there is an external field \mathbf{H}_{ext} , then the total field acting on the i th spin is

$$\mathbf{H} = \mathbf{H}_{eff} + \mathbf{H}_{ext} \quad (14)$$

Since \mathbf{M} is a paramagnetic function of \mathbf{H} :

$$\mathbf{M} = f(\mathbf{H}_{eff} + \mathbf{H}_{ext}) \quad (15)$$

where

$$\mathbf{H}_{eff} = \lambda \mathbf{M} \quad (16)$$

We can solve these two equations *self-consistently* for \mathbf{M} . Let's do some simple examples of this.

1. Suppose that \mathbf{H}_{ext} is small, and let us assume that \mathbf{M} and hence \mathbf{H}_{eff} will also be small. Then assuming that $\mathbf{M} \parallel \mathbf{H}_{ext} \parallel \mathbf{H}_{eff} \parallel \hat{z}$

$$\begin{aligned} M &= \chi_C H && \text{where } \chi_C = \text{Curie susceptibility} \\ &= \chi_C (H_{ext} + H_{eff}) \\ &= \chi_C H_{ext} + \chi_C \lambda M \end{aligned} \quad (17)$$

Solving for M yields

$$M = \frac{\chi_C}{1 - \lambda \chi_C} H_{ext} \quad (18)$$

Since $\chi = \partial M / \partial H_{ext}$, we get

$$\chi = \frac{\chi_C}{1 - \lambda \chi_C} \quad (19)$$

Putting $\chi_C = C/T$, where C is the Curie constant, gives the Curie-Weiss Law:

$$\chi(T) = \frac{C}{T - \lambda C} = \frac{C}{T - T_C} \quad (20)$$

where $T_C = \lambda C$. This reduces to the Curie law $\chi \cong C/T$ for $T \gg T_C$, but as we approach T_C from above, the susceptibility diverges. This indicates that at the transition temperature ($T = T_C$), the system can acquire a spontaneous magnetization even in the absence of an external field, i.e., it becomes ferromagnetic. If we plug in our expressions for λ and C :

$$\begin{aligned} \lambda &= \frac{2zJ}{ng^2\mu_B^2} \\ C &= \frac{n(g\mu_B)^2 S(S+1)}{3k_B} \end{aligned} \quad (21)$$

(The expression for C is from Reif Eq. (7.8.22). We will derive it later in this lecture.) We obtain

$$T_C = \lambda C = \frac{2zJS(S+1)}{3k_B} \quad (22)$$

where T_C is the Curie temperature. This is reasonable since the energy of a given spin S in the field of its neighbors is $\sim zJS^2$. Notice that T_C is proportional to the exchange energy J and to the number of neighbors z .

2. Below T_C , or in high fields above T_C , we can no longer use the Curie approximation $M = \chi_C H$. Rather we must use the full nonlinear expression which leads to the Brillouin function. (For $S = 1/2$, Brillouin function reduces to tanh.) The one-atom Hamiltonian is (again assuming that \mathbf{H}_{ext} , \mathbf{H}_{eff} , and \mathbf{M} to be along the z -axis)

$$\mathcal{H}_1 = -g\mu_B S_z H \quad H = H_{ext} + H_{eff} \quad (23)$$

and has eigenvalues

$$E_m = -g\mu_B mH \quad m = S, S-1, \dots, -S \quad (24)$$

The partition function is

$$\begin{aligned} Z &= \sum_m e^{-E_m/k_B T} \\ &= \sum_{m=-S}^S e^{g\mu_B mH/k_B T} \\ &= \sum_{m=-S}^S e^{mx/S} \quad x = \frac{g\mu_B SH}{k_B T} \text{ (dimensionless)} \\ &= \frac{\sinh\left(\frac{2S+1}{2S}x\right)}{\sinh\left(\frac{1}{2S}x\right)} \end{aligned} \quad (25)$$

The magnetization is

$$\begin{aligned} M &= n\langle\mu_z\rangle \\ &= ng\mu_B\langle S_z\rangle \\ &= \frac{ng\mu_B \sum_{m=-S}^S m e^{-E_m/k_B T}}{Z(x)} \\ &= \frac{ng\mu_B}{Z} \sum_{m=-S}^S m e^{mx/S} \\ &= ng\mu_B S \frac{\partial \ln Z}{\partial x} \end{aligned} \quad (26)$$

Using $\ln Z = \ln \left[\sinh\left(\frac{2S+1}{2S}x\right) \right] - \ln \left[\sinh\left(\frac{x}{2S}\right) \right]$, we get

$$M = ng\mu_B S B_S(x) \quad (27)$$

where the Brillouin function

$$B_S(x) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S} \coth\left(\frac{x}{2S}\right) \quad (28)$$

For $S = 1/2$,

$$B_{1/2}(x) = \tanh x \quad (29)$$

If we define a dimensionless field $h = g\mu_B H/k_B T$, then

$$M = ng\mu_B S B_S(hS) \quad (30)$$

Aside: Let us take a moment to derive the expression for the Curie constant C in Eq. (21). At high temperatures or small fields, $hS \ll 1$. For $x \ll 1$

$$B_S(x) \approx \frac{S+1}{3S}x \quad \text{for } x \ll 1 \quad (31)$$

Plugging this into Eq. (30) yields

$$M = \frac{1}{3}ng\mu_B hS(S+1) \quad (32)$$

Plugging in $h = g\mu_B H/k_B T$ gives

$$\begin{aligned} M &= \frac{ng^2\mu_B^2 S(S+1)}{3k_B T} H \\ &= \chi_C H \end{aligned} \quad (33)$$

where

$$\chi_C = \frac{C}{T} \quad \text{and} \quad C = \frac{n(g\mu_B)^2 S(S+1)}{3k_B} \quad (34)$$

This is where Eq. (21) came from.

Now back to mean field theory. Eq. (30) is a self-consistent equation for M because $H = H_{ext} + \lambda M$. To solve for M , some numerical or graphical method of solution must be employed. The graphical procedure of Weiss is probably the simplest method. To use this, rewrite the equation for M in terms of a reduced magnetization σ :

$$\sigma = \frac{M}{ng\mu_B S} = B_S(hS) \quad (35)$$

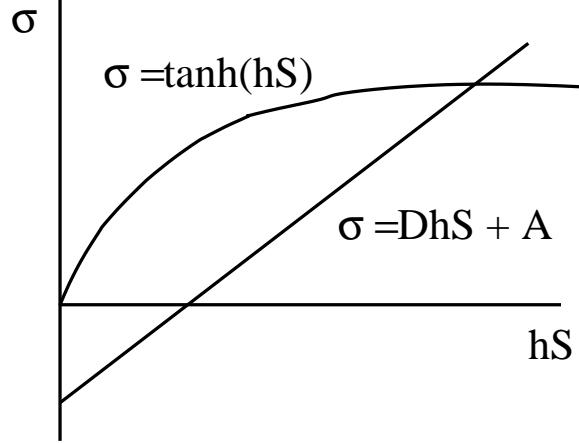
For $S = 1/2$,

$$\sigma = \tanh(hS) \quad (36)$$

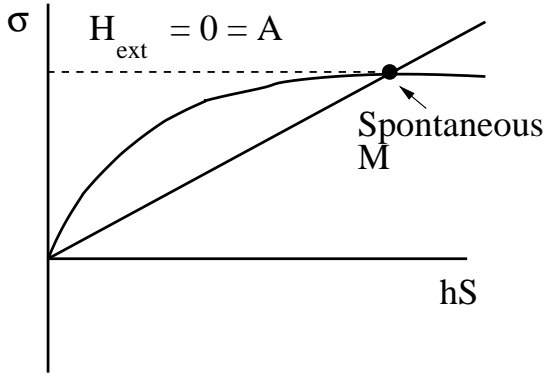
This gives one curve. The other curve comes from

$$\begin{aligned} hS &= h_{ext}S + h_{eff}S = \frac{g\mu_B S}{k_B T} (H_{ext} + H_{eff}) \\ H_{eff} &= \lambda M = \lambda ng\mu_B S\sigma = \frac{2zJ}{g\mu_B} S\sigma \quad \left(\lambda = \frac{2zJ}{ng^2\mu_B^2} \right) \\ hS &= \frac{g\mu_B S}{k_B T} H_{ext} + \frac{2zJS^2}{k_B T} \sigma \\ \sigma &= \frac{k_B T}{2zJS^2} hS - \frac{g\mu_B}{2zJS} H_{ext} \\ &= D \cdot hS + A \end{aligned} \quad (37)$$

This gives a straight line for σ versus hS . The intersection gives a self-consistent solution for σ and hence M .



The most important result of the Weiss theory is that when $H_{ext} = 0$ and the straight line passes through the origin, there is still a non-zero solution for σ , i.e., a spontaneous magnetization is predicted. The general behavior of the spontaneous magnetization can be inferred without extensive calculations. The slope of the straight line is proportional to T ($D \propto T$), and rotating the line about the origin corresponds to changing the temperature. When $T \rightarrow 0$, $\sigma \rightarrow 1$, and the material becomes completely magnetized. As T is increased, the spontaneous magnetization is reduced and finally vanishes when the slope of the line is equal to the initial slope of the Brillouin function. This occurs at the Curie temperature T_C that we found earlier.



We can solve for T_C by matching the slopes at $x = 0$ of the Brillouin function and the straight line:

$$B_S(x) \approx \frac{S+1}{3S}x \quad \text{for } x \ll 1 \quad (38)$$

The straight line at small x is given by

$$B_S(x = hS) = \sigma = \frac{k_B T}{2zJS^2}x \quad \text{if } H_{ext} = 0 \text{ and } x = hS \quad (39)$$

Matching the slopes at $T = T_C$ yields

$$\begin{aligned}\frac{k_B T_C}{2zJS^2} &= \frac{S+1}{3S} \\ T_C &= \frac{2zJS(S+1)}{3k_B}\end{aligned}\quad (40)$$

which is what we got before. We can use this to write a special equation of state for the spontaneous magnetization. For $H_{ext} = 0$,

$$\sigma = \frac{k_B T}{2zJS^2} hS \quad (41)$$

Solving for hS yields

$$\begin{aligned}hS &= \frac{2zJS^2\sigma}{k_B T} \\ &= \frac{3S}{(S+1)} \frac{T_C}{T} \sigma\end{aligned}\quad (42)$$

So at $H_{ext} = 0$, $\sigma = B_S(hS)$ becomes

$$\sigma = B_S\left(\frac{3S}{S+1} \frac{\sigma}{\tau}\right) \quad (43)$$

where $\tau = T/T_C$.

Temperature dependence of the magnetization:

$T \sim 0$ Mean field theory predicts

$$\sigma \simeq 1 - \frac{1}{S} \exp\left(-\frac{3}{S+1} \frac{T_C}{T}\right) + \dots \quad (44)$$

Experiment is closer to spin wave theory:

$$\sigma = 1 - AT^{3/2} - \dots \quad (45)$$

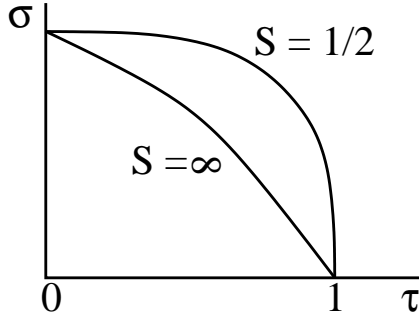
For $T \sim T_C^-$

$$\sigma \sim \left(\frac{T_C - T}{T_C}\right)^{1/2} \quad (46)$$

from mean field theory. In general one writes

$$M \sim \sigma \sim \left(\frac{T_C - T}{T_C}\right)^\beta \quad (47)$$

where β is a *critical exponent*. Experiment finds $\beta \sim 1/3$.



Appendix: Derivation of Quantum Mechanical Exchange

The origin of the ordering field is a quantum mechanical exchange effect. The simplest example of the exchange effect can be seen in the quantum mechanics of a system of 2 electrons. The Hamiltonian for the pair is

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \frac{e^2}{r_{12}} = \mathcal{H}_o + \frac{e^2}{r_{12}} \quad (48)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and \mathcal{H}_1 and \mathcal{H}_2 are the Hamiltonians of electron 1 and electron 2, respectively. The electrons are either in a singlet state or a triplet state:

$$\begin{aligned} \psi_S &= \frac{1}{\sqrt{2}} [\phi_i(1)\phi_j(2) + \phi_i(2)\phi_j(1)] \chi_o \\ \psi_T &= \frac{1}{\sqrt{2}} [\phi_i(1)\phi_j(2) - \phi_i(2)\phi_j(1)] \chi_1 \end{aligned} \quad (49)$$

where the singlet spin wavefunction ($S = 0$) is

$$\chi_o = \frac{1}{\sqrt{2}} [\uparrow\downarrow - \downarrow\uparrow] \quad (50)$$

and the triplet spin wavefunction ($S = 1$) is

$$\chi_1 = \begin{cases} \uparrow\uparrow & S_z = 1 \\ \frac{1}{\sqrt{2}}[\uparrow\downarrow + \downarrow\uparrow] & S_z = 0 \\ \downarrow\downarrow & S_z = -1 \end{cases} \quad (51)$$

Without the Coulomb interaction, the singlet and triplet are degenerate (have equal energy):

$$\mathcal{H}_o \psi_{T,S} = E_{T,S}^o \psi_{T,S} \quad (52)$$

where $E_T^o = E_S^o = E_i + E_j$. If we include the Coulomb interaction e^2/r_{12} using first order perturbation theory, then

$$E_S = E^o + \langle \psi_S | \frac{e^2}{r_{12}} | \psi_S \rangle = E^o + C_{ij} + J_{ij} \quad (53)$$

$$E_T = E^o + \langle \psi_T | \frac{e^2}{r_{12}} | \psi_T \rangle = E^o + C_{ij} - J_{ij} \quad (54)$$

where

$$C_{ij} = \int \phi_i^*(1)\phi_j^*(2)\frac{e^2}{r_{12}}\phi_i(1)\phi_j(2)d^3r + (i \leftrightarrow j) \quad (55)$$

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2)\frac{e^2}{r_{12}}\phi_i(2)\phi_j(1)d^3r + (i \leftrightarrow j) \quad (56)$$

C_{ij} is the average Coulomb interaction between 2 electrons in states i and j . J_{ij} is the exchange energy of 2 electrons in states i and j . Thus the singlet and triplet energies are now different; whether the singlet state or the triplet state has the lower energy and is the ground state depends on the sign of J_{ij} . In this particular case, J_{ij} is positive and the triplet has lower energy because the antisymmetric spatial wavefunction weakens the Coulomb repulsion. In more general cases, e^2/r_{12} is replaced by $V(\mathbf{r}_1, \mathbf{r}_2)$, and J_{ij} can be either positive or negative.

The exchange energy can be rewritten in terms of a spin exchange operator

$$P^\sigma = \frac{1}{2}(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2) \quad (57)$$

which has the property

$$P^\sigma \chi_{S^{m_s}}(\tau_1, \tau_2) = \chi_{S^{m_s}}(\tau_2, \tau_1) \quad (58)$$

where $\chi_{S^{m_s}}(\tau_1, \tau_2)$ is the spin wavefunction of 2 particles with spin coordinates τ_1 and τ_2 . To prove this, note that for $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$

$$\mathbf{S}^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \quad (59)$$

$$\mathbf{S}_1 \cdot \mathbf{S}_2 = \frac{1}{2}[\mathbf{S}^2 - \mathbf{S}_1^2 - \mathbf{S}_2^2] \quad (60)$$

Since $\mathbf{S} = \vec{\sigma}/2$ and $S_1 = S_2 = 1/2$, $S_1^2 = S_1(S_1 + 1) = 3/4$. So

$$\begin{aligned} \frac{1}{4}\vec{\sigma}_1 \cdot \vec{\sigma}_2 &= \frac{1}{2}\left[S(S+1) - \frac{3}{2}\right] \\ \vec{\sigma}_1 \cdot \vec{\sigma}_2 &= 2\left[S(S+1) - \frac{3}{2}\right] = \begin{cases} -3 & \text{for } S = 0 \\ 1 & \text{for } S = 1 \end{cases} \end{aligned} \quad (61)$$

So

$$\begin{aligned} P^\sigma \chi_{S=1}^{m_s}(\tau_1, \tau_2) &= \frac{1}{2}[1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2] \chi_{S=1}^{m_s}(\tau_1, \tau_2) \\ &= \chi_{S=1}^{m_s}(\tau_1, \tau_2) \\ &= \chi_{S=1}^{m_s}(\tau_2, \tau_1) \end{aligned} \quad (62)$$

and

$$\begin{aligned} P^\sigma \chi_{S=0}^{m_s=0}(\tau_1, \tau_2) &= \frac{1}{2}[1 - 3] \chi_{S=0}^{m_s=0}(\tau_1, \tau_2) \\ &= -\chi_{S=0}^0(\tau_1, \tau_2) \\ &= \chi_{S=0}^0(\tau_2, \tau_1) \end{aligned} \quad (63)$$

Therefore,

$$P^\sigma \chi_S^{m_s}(\tau_1, \tau_2) = \chi_S^{m_s}(\tau_2, \tau_1) \quad (64)$$

Thus we can write

$$\begin{aligned} E &= E^o + C_{ij} - J_{ij} \langle \chi_S^{m_s} | P^\sigma | \chi_S^{m_s} \rangle \\ &= E^o + C_{ij} - J_{ij} \left[\frac{1}{2} (1 + \langle \vec{\sigma}_1 \cdot \vec{\sigma}_2 \rangle) \right] \\ &= \begin{cases} E_S & \text{if } S = 0 \\ E_T & \text{if } S = 1 \end{cases} \end{aligned} \quad (65)$$

This implies that we can write the Hamiltonian in the form

$$\mathcal{H} = \text{const} - \frac{1}{2} J_{ij} \vec{\sigma}_1 \cdot \vec{\sigma}_2 \quad (66)$$

We now make a rather bold leap of faith and assume that we can write a similar Hamiltonian for a system with many electrons.

$$\mathcal{H} = -\frac{1}{2} \sum_{i>j} J_{ij} \vec{\sigma}_i \cdot \vec{\sigma}_j \quad (67)$$

This is the *Heisenberg Hamiltonian* and J_{ij} are called the exchange constants. Usually one writes

$$\mathcal{H} = -2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (68)$$

where the factor of 4 is from $(S = \sigma/2)^2$.