Lecture 18

Magnetism, Magnetic Order

Love thy neighbors

SI and CGS

- Magnetic susceptibility
  - SI : $\chi = \mu_0 M/H$ or $\mu_0\, dM/dH$
  - CGS : $\chi = M/H$ or dM/dH
- Constitutive equations
  - SI : $B = \mu_0(H + M)$
  - CGS : $B = H + 4\pi M$
- Will use the SI unit in this note (see Kittel for both units).

Origin of Magnetic Moment in Solids

- Electrons are the main source

  (Nuclear spins do come in handy as in NMR)

- Magnetic moment
  - $\boldsymbol{\mu} = -\mu_B (\mathbf{L} + g_0 \mathbf{S})$, $g_0 = 2.0023\ldots \approx 2$
  - $\mu_B = e\hbar/(2m)$
    - μ_B = 9.27e-24 J/T (SI) or 5.8e-9 eV/gauss
    - For nucleons, reduction by ~ 2000
    - Remember, B field ~ 100 T = 1e6 gauss is the strongest field that one can generate, so magnetic perturbation energies are quite small.

Some Atomic Physics …

- **Spin-orbit coupling**:
  - H_{LS} **= L** · **S** $e^2/(r^3 8\pi\varepsilon_0 m^2 c^2)$
  - Goes like ~ α^2 x unperturbed energy
  - The heavier the atom, the greater $\langle H_{LS} \rangle$
  - The closer the orbital is to the atom, the greater $\langle H_{LS} \rangle$
  - Quite important for the band structure of semiconductors (44 meV for Si, 0.34 eV for GaAs)
- **Zeeman interaction**:
  - $H_B = -\mu \cdot \mathbf{B} = -\mu_B (\mathbf{L} + 2\,\mathbf{S}) \cdot \mathbf{B}$
- For very light atoms (Li, e.g.), the Zeeman term can be more important than the spin-orbit coupling.
- **For most solid problems, the spin-orbit coupling is more important than the Zeeman term**.
  - Treat spin-orbit first, and then, treat Zeeman as a perturbation.
  - Good Quantum Numbers: J, L, S, J_z
  - $\langle H_B \rangle = g(L,S,J)\, \mu_B J_z B$ (**g: Lande g-factor**; see A&M, Sakurai)

$\mu_{eff} = g\, \mu_B J_z$

Ref: QM books (Griffiths, Sakurai …)

Hund's Rule for Atomic Spectra

- Empirical rule that works pretty well for 3d Transition metal (TM) and 4f rare earth (RE) ions
- Many electrons in an un-filled orbital
  - First rule: maximize S
  - Second rule: maximize L
  - Third rule: J = |L-S| if less than half full and J = L+S if more than half full
  - Notation: $^{2s+1}L_J$
- E.g., V^{3+} : $3d^2$ $^3F_2$, Fe^{2+} : $3d^6$ $^5D_4$, Mn^{2+} : $3d^5$ $^6S_{5/2}$
- Roughly, the physics is due to Coulomb interaction and spin-orbit interaction

Ref: Slater "Quntum Theory of Atomic Structure," Landau and Lifshitz

Magnetism – Classical physics can't do it

Bohr-von Leeuwen theorem

According to this theorem, Classical mechanics cannot explain magnetism. It is very easy to prove it. From Stat-Mech, recall that the partition function for a classical system is given as

$$Z(\vec{H}) \propto \int d\vec{r}\, d\vec{p}\, \exp(-\beta \mathcal{H}(\vec{r}, \vec{p}))$$

But, $\mathcal{H}(\vec{r}, \vec{p}) = \mathcal{H}_0\left(\vec{r}, \vec{p} - \frac{q}{c}\vec{A}(\vec{r})\right)$, where $\mathcal{H}_0$ ($\mathcal{H}$) is the Hamiltonian function without (with) the $\vec{H}$ field, and $\vec{H} = \vec{\nabla} \times \vec{A}$. Notice however the integral over $\vec{p}$ can be simply shifted so that

$$Z(\vec{H}) \propto \int d\vec{r}\, d\vec{p}'\, \exp(-\beta \mathcal{H}_0(\vec{r}, \vec{p}'))$$

Thus, we just showed that $Z(\vec{H}) = Z(\vec{H} = 0)$. Since the partition function does not depend on the applied field, and so $M = -\frac{1}{V}\frac{\partial F}{\partial H} = \frac{k_B T}{V}\frac{\partial \ln Z}{\partial H} = 0$. Therefore, the system has no magnetic response, and thus no magnetism.
Also, the majority of magnetism arises due to the electron spin, which is absent in Classical Mechanics.

Curie Paramagnetism

- Localized magnetic moments in response to external B field
- $M = \chi H$
- Curie law at high T, small B: $\chi = C/T$
  - $C = N p^2 \mu^2_B \mu_0 / (3 k_B)$ (N is # of magnetic moments)
  - $p = g [J(J+1)]^{1/2}$
- Saturation at low T, large B: $M = Ng\mu_B J$
- p agrees well for RE, but not so for TM
- For TM ions, $p = 2 [S(S+1)]^{1/2}$ works much better!?

Quenching of Orbital Moment in Transition Metal Ions in Crystal

- Empirically observed (Kittel, p. 308)
- Effect of Crystal Field (large ~ 1 eV in TM ions)
- L_z is not a good quantum number
- $< L_z >$ (also for x,y) is often zero

Pauli Para-magnetism of Metals

- Response of Fermi sea to the magnetic field
- Spin-up electron's energy goes up and spin-down … down, both by $\mu_B B$
- $M = \mu_B(n_\uparrow - n_\downarrow) = \mu_B^2 g(E_F) B$ (g is per volume, but for both spins)
- $\chi = M / H \approx \mu_0 \mu_B^2 g(E_F)$ (T independent)
- $\chi \sim \mu_0 \mu_B^2 N/E_F$ (N is volume density), i.e. weakened by T/T_F (quantum behavior – only those at E_F respond) compared to Curie susceptibility (classical behavior – all spins respond)

Diamagnetism

- Lenz's law
- Landau Diamagnetism
  - Orbital Motion of Electrons
  - For free electron, $\chi_{Landau} = - \chi_{Pauli}/3$
  - For effective mass m*, $\chi_{Landau} / \chi_{Pauli} \sim (m/m^*)^2$
    i.e. $|\chi_{Landau}| >> \chi_{Pauli}$ (semi-cond) and $|\chi_{Landau}| << \chi_{Pauli}$ (heavy Fermion)
- Larmor (Langevin) Diamagnetism due to closed shell ions ($\mathbf{A} = -\mathbf{r}\times\mathbf{B}/2$, $H = (\mathbf{p}+e\mathbf{A})^2/2m$, The last term of $H \sim r^2B^2$)
- For non-magnetic materials, often it is necessary to consider <u>all</u> susceptibilities (Pauli, Landau, Larmor, and Curie – often due to magnetic impurities)

Different Kinds of Magnetic Order

- **Ferro-magnetism** (Fe, CrO_2, EuO, etc.)
- Anti-ferromagnetism (MnO, FeF_2, HTSC cuprates, etc.)
- Ferri-magnetism (Fe_3O_4) …
- Note

1. Magnetic orders happen at fairly high temperatures (100 K ~ 1000 K) – i.e. internal field is very high due to <u>Coulomb interaction</u>
2. The above are B=0 properties, while the following designate response to finite B:
   - Para-magnetism (Curie, Van Vleck, Pauli)
   - Dia-magnetism (Larmor, Landau, London)

Interaction between Magnetic Ions

- Dipole-dipole interaction is very small

$$\vec{B} = \frac{3(\vec{m}\cdot\hat{r})\hat{r} - \vec{m}}{r^3} \quad (cgs)$$

$$\mu_B \approx 6\times10^{-9}\ eV/gauss \approx 9\times10^{-21}\ erg/gauss$$

$$B \sim \frac{\mu_B}{r^3} \sim \frac{9\times10^{-21}}{(3\mathring{A})^3} \sim \frac{10^{-21}}{3\times10^{-24}} \sim 1000\ gauss$$

$$E \sim \mu_B B \sim 6\times10^{-6}\ eV \sim 0.006\ meV \sim O(0.01)\ K$$

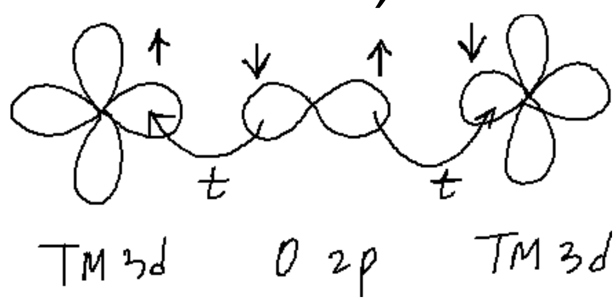
- Magnetic exchange energy results from Coulomb interactions: hopping (t) and exchange interactions
- Two most important Hamiltonians:

Heisenberg $H = -\sum_{\langle i,j\rangle} J_{ij}\, \vec{S}_i \cdot \vec{S}_j$

Hubbard H = Kinetic Energy + Exchange Coulomb Energy

Sign of J in Heisenberg Model

- Positive like "Hund's rule" ($J > 0$): Equal spins repel less
- **Super-Exchange** ($J < 0$): TM ions (such as ions of Fe, Mn, Cu etc) interact via anions



- Double exchange ($J > 0$), RKKY (J can be random), …

Ferromagnetism due to local spins

- Consider Heisenberg Hamiltonian with only nearest-neighbor interaction (now <i,j> means only nearest neighbor pairs, not all possible pairs) and J > 0

$$H = -J \sum_{\langle i,j \rangle} \vec{S_i} \cdot \vec{S_j}$$

- This Hamiltonian is very difficult to solve. One can however show that all spins pointing in the same direction is the lowest energy state. For instance for spin ½, it is easy to show

$$H|\psi\rangle = -NJ/4|\psi\rangle \qquad |\psi\rangle = |\uparrow\uparrow\uparrow \cdots \uparrow\uparrow\uparrow\rangle$$

where z direction is any random direction. (Hint: use $S_x = \frac{1}{2}(S_+ + S_-)$ $S_y = -\frac{i}{2}S_+ + \frac{i}{2}S_-$)

Ferromagnetism due to local spins

- Clearly the ground state is one in which all spins are aligned (symmetry breaking) and the excited state is in one in which spins are flipped (magnon or spin wave)
- At finite T, each spin will "fluctuate" around its mean value (even at T=0 due to quantum fluctuations)
- An elementary approach is then to ignore these fluctuations and apply a "mean field" theory

Mean field theory of FM (Weiss)

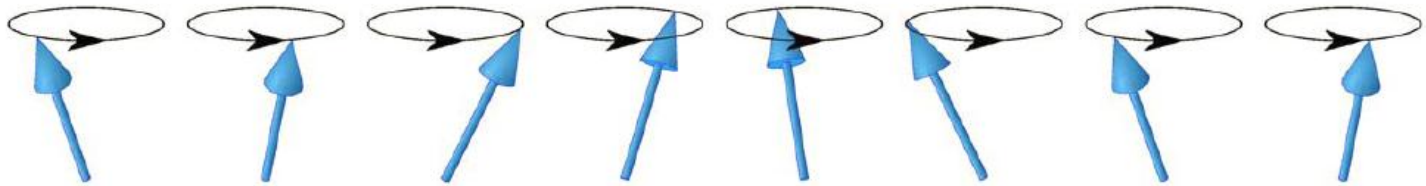
- There is an enormous internal field due to magnetization ($\lambda >> 1$): $\lambda \mu_0 \vec{M}$ $\quad \vec{B} = \lambda \mu_0 \vec{M} + \vec{B}_{loc}$
- At high T, Curie-Weiss Law: $\chi = \frac{C}{T - T_c}$
- At T < Tc, spontaneous magentization
- T = 0: Saturation without any external field $M = N\mu$
- Provides basic picture for the FM transition but …
  - T-dependence near Tc (wrong):

    $$M \propto \left(1 - \frac{T}{T_c}\right)^{\frac{1}{2}} \qquad \chi \propto (T - T_c)^{-1}$$

  - T-dependence near T = 0 (wrong):

    $$M = N\mu\left(1 - 2\exp\left(-\frac{2T_c}{T}\right)\right)$$

Spin Wave and Bloch $T^{3/2}$ law in FM



http://upload.wikimedia.org/wikipedia/commons/0/01/FerromagneticMagnon.svg

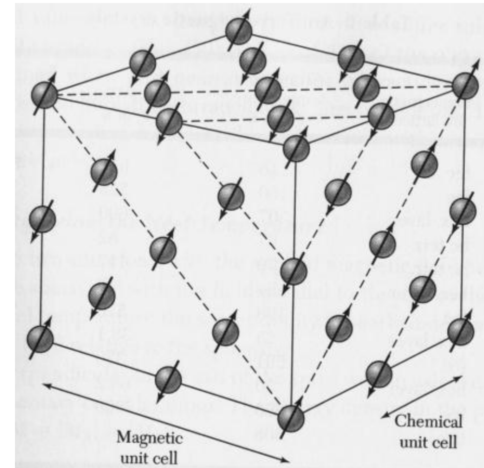
- Quantum Mechanically, spin wave means excited states with one spin flipped
- Easiest way to consider this is to do Classical Mechanics (like phonon problem)
- We know that k=0 solution must exist with energy = 0 (like the acoustic phonon case)
- FM spin wave has the property: $\omega \propto k^2$
- This leads to Bloch's law near T=0:

$C \propto T^{3/2}$ $\quad\quad$ $\vec{M}$ reduction $\sim T^{3/2}$

Antiferromagnetism

- Spins align anti-parallel to each other (J < 0 due mostly to the Anderson super-exchange)
- Different from FM in that
  - AFM state is not an eigenstate
  - Not even ground state (!)
  - But thermodynamically favored state at $T<T_N$
  - Magnetic unit cell differs from chemical unit cell
  - Spin wave is <u>really</u> like phonon:

$$\omega \approx \omega_{ex} |ka| \qquad k \to 0$$



Mn^{2+} ions in MnO (from Kittel)

High T susceptibility of FM or AFM due to local spins

$\chi \sim 1/(T - \Theta)$
(FM: $\Theta \sim O(T_C)$, <u>Curie Temperature</u>)

$\chi \sim 1/(T + \Theta)$
(AFM: $\Theta \sim O(T_N)$, <u>Néel Temperature</u>)

Θ is not exactly T_C (or T_N) because the theory presented here is very simple (only nearest neighbor interaction and mean-field)

Itinerant Ferromagnetism

- One of the mechanism for metallic FM (as in Fe)
- Due to exchange Coulomb interaction
- Exchange interaction favors spin polarization but kinetic energy favors no spin polarization **(competition)**
- The onset of the FM is given by Stoner criterion in perturbation MF theory

$$\frac{g(\varepsilon_F)}{N} \cdot U = 1$$

Stoner Ferromagnetism

- Just like Pauli Para-magnetism theory, but with internal field

$$\varepsilon_{\vec{k}\uparrow} = \varepsilon_{\vec{k}} + U n_{\downarrow} \quad \text{Exchange energy } U > 0$$

$$\varepsilon_{\vec{k}\downarrow} = \varepsilon_{\vec{k}} + U n_{\uparrow}$$

$$M = \mu_B (n_{\uparrow} - n_{\downarrow})$$

$$n = n_{\uparrow} + n_{\downarrow}$$

$n, n_{\uparrow}, n_{\downarrow}$: # densities

$$\varepsilon_{k\uparrow} = \varepsilon_{\vec{k}} + U \cdot \frac{n}{2} - U \frac{M}{2\mu_B}$$

$$\varepsilon_{k\downarrow} = \varepsilon_{\vec{k}} + U \cdot \frac{n}{2} + U \cdot \frac{M}{2\mu_B}$$

- Self-consistency (source M is the same as the result, as in Weiss MF theory) – left for reader – leads to "Stoner Criterion"

$$\frac{g(\varepsilon_F)}{N} \cdot U = 1$$