

Lecture 19 (March 4)

Sources of magnetism:

(i) magnetic moments due to electric currents:

$$\vec{m} = \frac{1}{2c} \int d^3x \vec{x} \times \vec{j}(\vec{x})$$

(ii) intrinsic spin:

$$\vec{m} = g \mu_0 \vec{S} / \hbar$$

Here $\mu_0 = q \hbar / 2mc$ is the magneton. For the electron, $q = -e < 0$ and $\mu_{e^-} = -\mu_B$ with $\mu_B = e \hbar / 2m_e c = 5.788 \times 10^{-9} \text{ eV/G}$.

Note $\mu_B / k_B = 6.717 \times 10^{-5} \text{ G/K}$ so for electrons setting $\mu_B H = k_B T$ with $T = 1 \text{ K}$ gives $H = 1.489 \times 10^4 \text{ G} \approx 15 \text{ T}$.

Single electron Hamiltonian:

$$H = \underbrace{\frac{(\vec{p} + \frac{e}{c} \vec{A})^2}{2m}}_{\text{kinetic}} + \underbrace{V(\vec{x})}_{\text{potential}} + \underbrace{\frac{e \hbar}{2m c} \vec{\sigma} \cdot \vec{H}}_{\text{Zeeman}} + \underbrace{\frac{\hbar}{4m^2 c^2} \vec{\sigma} \cdot \nabla V \times (\vec{p} + \frac{e}{c} \vec{A})}_{\text{spin-orbit}}$$

Where does this come from? From the Dirac equation:

$$+ \frac{\hbar^2}{8m^2 c^2} \nabla^2 V + \frac{[(\vec{p} + \frac{e}{c} \vec{A})^2]^2}{8m^3 c^2} + \dots$$

Darwin $\sigma(1/(mc^2)^2)$

$$i \hbar \frac{\partial \Psi}{\partial t} = \begin{pmatrix} mc^2 + V & c \vec{\sigma} \cdot \vec{\pi} \\ c \vec{\sigma} \cdot \vec{\pi} & -mc^2 + V \end{pmatrix} \Psi$$

Dirac spinor
(4 components)

$$\vec{\pi} = \vec{p} + \frac{e}{c} \vec{A}$$

A canonical transformation, the Foldy - Wouthuysen transformation, is invoked to separate the upper two components from the lower two components (see §14.11), i.e. $H \rightarrow e^{iS} H e^{-iS}$.

The Zeeman term is more properly written as

$$H_z = g \mu_B \vec{S} \cdot \vec{H} / \hbar \approx \mu_B \vec{\sigma} \cdot \vec{H}$$

where $\vec{S} = \frac{1}{2} \hbar \vec{\sigma}$ and

$$g = 2 \cdot \left\{ 1 + \frac{\alpha}{2\pi} + O(\alpha^2) \right\}$$

"tree level"

radiative corrections (from QED)

where $\alpha = e^2 / \hbar c \approx 1/137$ is the fine structure constant.

Response:

$$\vec{M} = -\frac{1}{V} \frac{\partial F}{\partial \vec{H}} = \text{magnetization}$$

$$\chi_{\alpha\beta}(\vec{x}, \vec{x}') = -\frac{1}{V} \frac{\partial^2 F}{\partial H^\alpha(\vec{x}) \partial H^\beta(\vec{x}')} = \text{susceptibility}$$

$$\chi_{\alpha\beta}(\vec{x}t, \vec{x}'t') = \frac{\delta \langle M^\alpha(\vec{x}, t) \rangle}{\delta H^\beta(\vec{x}', t')} = \text{dynamical susceptibility}$$

Bohr - von Leeuwen theorem: absence of orbital magnetism in classical physics:

$$Z(\vec{A}) = \int \frac{d^N \vec{x} d^N \vec{p}}{h^{dN}} e^{-\beta H(\{\vec{p}_i + \frac{q}{c} \vec{A}(\vec{x}_i), \vec{x}_i\})} = Z(0)$$

Non-orbital magnetism is classically allowed (e.g., Ising model).

Basic atomic physics: Start with

$$H_{\text{electron}} = \frac{\vec{\pi}^2}{2m} + V(\vec{x}) + \mu_B \vec{H} \cdot \vec{\sigma} + \frac{\hbar}{4m^2c^2} \vec{\sigma} \cdot \vec{\nabla} V \times \vec{\pi}$$

where $\vec{\pi} = \vec{p} + \frac{e}{c} \vec{A}(\vec{x})$. In a crystal, $V(\vec{x})$ has discrete point group symmetries. For an isolated atom, $V(\vec{x})$ is isotropic, i.e. $V(\vec{x}) = V(r = |\vec{x}|)$. Then, taking $\vec{A} = \frac{1}{2} \vec{H} \times \vec{r}$,

$$H_{so} = \frac{1}{2m^2c^2} \vec{S} \cdot \vec{\nabla} V \times (\vec{p} + \frac{e}{2c} \vec{H} \times \vec{r})$$

$$\vec{\nabla} V = \frac{\partial V}{\partial r} \hat{r} = \frac{1}{r} \frac{\partial V}{\partial r} \vec{r}$$

$$H_{so} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \vec{S} \cdot (\vec{r} \times \vec{p} + \frac{e}{2c} \vec{r} \times (\vec{H} \times \vec{r}))$$

$$= \frac{1}{2m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \vec{S} \cdot \vec{l} + \frac{\mu_B}{\hbar} \frac{rV'(r)}{2mc^2} \vec{S} \cdot [\vec{H} - \hat{r}(\vec{H} \cdot \hat{r})]$$

Next, expand

smaller than $\mu_B \vec{H} \cdot \vec{\sigma}$ by $\frac{rV'(r)}{mc^2}$

$$\frac{\vec{\pi}^2}{2m} = \frac{\vec{p}^2}{2m} + \frac{e}{2mc} \vec{H} \cdot \vec{l} + \frac{e^2}{8mc^2} (\vec{H} \times \vec{r})^2$$

where $\vec{l} = \vec{r} \times \vec{p}$. The Darwin term is

$$\frac{\hbar^2}{8m^2c^2} \nabla^2 V = \frac{Z\pi e^2 \hbar^2}{2m^2c^2} \delta(\vec{r})$$

Since $V(\vec{r}) = -Ze^2/r$, Thus, this adds a s-wave energy shift

$$\Delta E_{s\text{-wave}} = \underbrace{\pi a^2 Z}_{10^{-4}} a_B^3 |\psi(0)|^2 \cdot \underbrace{\frac{e^2}{2a_B}}_{1Ry = 13.6\text{ eV}}$$

Many electrons:

$$H = \sum_{j=1}^N \left\{ \frac{\vec{p}_j^2}{2m} - \frac{Ze^2}{r_j} \right\} + \sum_{j=1}^N \zeta(r_j) \vec{l}_j \cdot \vec{s}_j \\ + \sum_{j=1}^N \left\{ \frac{\mu_B}{\hbar} (\vec{l}_j + 2\vec{s}_j) \cdot \vec{H} + \frac{e^2}{8mc^2} (\vec{H} \times \vec{r}_j)^2 \right\} + \sum_{i < j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

with

$$\zeta(r) = \frac{Ze^2}{2m^2c^2} \cdot \frac{1}{r^3} = \frac{Z}{\hbar^2} \alpha^2 \left(\frac{a_B}{r} \right)^3 \cdot \frac{e^2}{2a_B}$$

Zero external field: We have

$$H = \sum_{j=1}^N \left\{ \frac{\vec{p}_j^2}{2m} - \frac{Ze^2}{r_j} + \zeta(r_j) \vec{l}_j \cdot \vec{s}_j \right\} + \sum_{i < j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

How to treat e-e interaction term? Hartree-Fock:

$$\Psi_{\sigma_1 \dots \sigma_N}(\vec{r}_1, \dots, \vec{r}_N) = A \left[\varphi_1(\vec{r}_1, \sigma_1) \dots \varphi_N(\vec{r}_N, \sigma_N) \right]$$

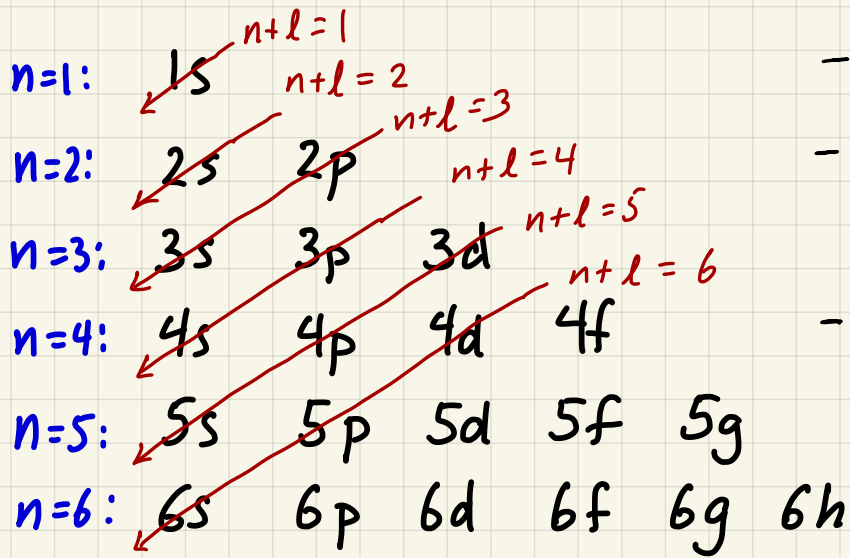
↖ antisymmetrizer

As we have discussed, the important physics introduced by HF is that of **screening**. We still assume spatial isotropy, meaning the states $\varphi(\vec{r})$ can be labeled by l, m, m_s , and a principal quantum number n . Screened potential:

$$V(r) = \begin{cases} -Ze^2/r & , r \rightarrow 0 \\ -Ce^2a_B^3/r^4 & , r \rightarrow \infty \end{cases}$$

For hydrogenic atoms, $\epsilon_{nl} = \epsilon_n$ independent of l . But for

a screened potential, for a given n , smaller l means closer to nucleus, lower energy. We discussed the Aufbau principle:



heuristic:

- fill lower $(n+l)$ values first
- for equal $(n+l)$, fill the lower n states first
- (n, l) defines a shell with $(2s+1)(2l+1) = 4l+2$ states

Hund's rules:

Electronic configuration of C: $1s^2 2s^2 2p^2 = [\text{He}] 2s^2 2p^2$

There are six states for the 2p orbital: $\{p_x, p_y, p_z\} \times \{\uparrow, \downarrow\}$

Number of possible states: $\binom{6}{2} = 15$.

Quantum numbers: L, S, J with $\vec{J} = \vec{L} + \vec{S} \Rightarrow J \in \{|L-S|, \dots, L+S\}$

Standard notation: $^{2S+1}L_J$ is called a term

$$2S+1 = 1, 2, 3, \dots$$

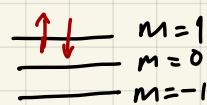
$$L = S, P, D, F, \dots$$

$$J = 0, \frac{1}{2}, 1, \dots$$

$$15 = \binom{6}{2} \text{ states}$$



carbon 2p levels:

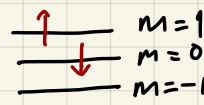


$$L=2$$

$$S=0$$

$$J=2$$

$${}^1D_2 (5)$$



$$L=1$$

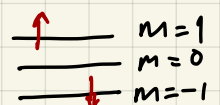
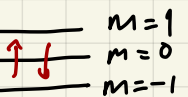
$$S=1$$

$$J=0, 1, 2$$

$${}^3P_0 (1)$$

$${}^3P_1 (3)$$

$${}^3P_2 (5)$$



$$L=0$$

$$S=0$$

$$J=0$$

$${}^1S_0 (1)$$

So for carbon there are five terms and 15 states.

Which term has the lowest energy? Use Hund's rules:

(1) Maximize S

(2) Maximize L

(3) If incomplete shell $\leq \frac{1}{2}$ -filled, $J = |L - S|$ (min)

If incomplete shell $> \frac{1}{2}$ -filled, $J = L + S$ (max)

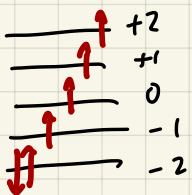
Carbon: (1) $\Rightarrow S = 1 \Rightarrow L = P$

(2) doesn't give any new info, since L is fixed

(3) $2p^2$ is less than half-filled $\Rightarrow J = 0$

So we conclude the ground state term of C is 3P_0 .

Another example: $Fe^{2+} = [Ar]4s^0 3d^6$

(1)  $S = 2$ (2) $M_{max} = 2 \Rightarrow L = 2$

(3) $> \frac{1}{2}$ -filled $\Rightarrow J = L + S = 4$ term is 5D_4

Hund's rules are, like the Aufbau principle, heuristics and not rigorous. Briefly they are justified by the following considerations:

#1: We maximize S because the spatial part of the WF is then "most antisymmetric", which reduces Coulomb repulsion

Shell:	1s	2s	2p	3s	3p	4s	3d	4p	5s
Termination:	² He	⁴ Be	¹⁰ Ne	¹² Mg	¹⁸ Ar	²⁰ Ca	³⁰ Zn	³⁶ Kr	³⁸ Sr
Shell:	4d	5p	6s	4f	5d	6p	7s	5f/6d	
Termination:	⁴⁸ Cd	⁵⁴ Xe	⁵⁶ Ba	⁷⁰ Yb	⁸⁰ Hg	⁸⁶ Rn	⁸⁸ Ra	¹⁰² No	

Table 14.1: Rough order in which shells of the Periodic Table are filled.

The 3d transition metal series ([Ar] core additions)					
Element (A^Z)	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵
Configuration	4s ² 3d ¹	4s ² 3d ²	4s ² 3d ³	4s ¹ 3d ⁵	4s ² 3d ⁵
Element (A^Z)	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰
Configuration	4s ² 3d ⁶	4s ² 3d ⁷	4s ² 3d ⁸	4s ¹ 3d ¹⁰	4s ² 3d ¹⁰

Table 14.2: Electronic configuration of 3d-series metals.

n_p	0	1	2	3	4	5	6								
L	0	1	1	0	1	1	0								
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	1	$\frac{1}{2}$	0								
J	0	$\frac{1}{2}$	0	$\frac{3}{2}$	2	$\frac{3}{2}$	0								
n_d	0	1	2	3	4	5	6	7	8	9	10				
L	0	2	3	3	2	0	2	3	3	2	0				
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	2	$\frac{3}{2}$	1	$\frac{1}{2}$	0				
J	0	$\frac{3}{2}$	2	$\frac{3}{2}$	0	$\frac{5}{2}$	4	$\frac{9}{2}$	4	$\frac{5}{2}$	0				
n_f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
L	0	3	5	6	6	5	3	0	3	5	6	6	5	3	0
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$	2	$\frac{5}{2}$	3	$\frac{7}{2}$	3	$\frac{5}{2}$	2	$\frac{3}{2}$	1	$\frac{1}{2}$	0
J	0	$\frac{5}{2}$	4	$\frac{9}{2}$	4	$\frac{5}{2}$	0	$\frac{7}{2}$	6	$\frac{15}{2}$	8	$\frac{15}{2}$	6	$\frac{7}{2}$	0

Table 14.3: Hund's rules applied to p, d, and f shells.

#2: We maximize L because this expands the electron cloud, further reducing Coulomb repulsion

#3: The Wigner-Eckart theorem says we may replace

$$H_{so} = \sum_{j=1}^N \zeta(r_j) \vec{l}_j \cdot \vec{s}_j \rightarrow \Lambda \vec{L} \cdot \vec{S}$$

Since $\vec{J} = \vec{L} + \vec{S}$, we have $\vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$ and

$$H_{so,eff} = \frac{1}{2} \Lambda \hbar^2 (J(J+1) - L(L+1) - S(S+1))$$

and thus $E(N, L, S, J) - E(N, L, S, J-1) = \Lambda \hbar^2 J$.

• $\leq \frac{1}{2}$ -filled ($N \leq 2L+1$): $\Lambda > 0 \Rightarrow J = |L-S|$

• $> \frac{1}{2}$ -filled ($N > 2L+1$): $\Lambda < 0 \Rightarrow J = L+S$

• Magnetic properties of atoms and ions:

To second order in the field \vec{H} , the atomic energies are

$$\begin{aligned} \Delta E_n(\vec{H}) = E_n(\vec{H}) - E_n(0) &= \frac{\mu_B}{\hbar} \vec{H} \cdot \langle n | \vec{L} + 2\vec{S} | n \rangle + \frac{c^2}{8mc^2} \langle n | \sum_{j=1}^N (\vec{H} \times \vec{r}_j)^2 | n \rangle \\ &+ \frac{\mu_B^2}{\hbar^2} H^\alpha H^\beta \sum_{n'}^{n' \neq n} \frac{\langle n | L^\alpha + 2S^\alpha | n' \rangle \langle n' | L^\beta + 2S^\beta | n \rangle}{E_n - E_{n'}} + \mathcal{O}(H^3) \end{aligned}$$

Filled shells at $T=0$: Here we have $|n\rangle = |G\rangle$ (ground state) for which $\vec{L}|G\rangle = \vec{S}|G\rangle = \vec{J}|G\rangle = 0$.

Thus, $\Delta E_0(\vec{H}) = \frac{e^2 \vec{H}^2}{12mc^2} \langle G | \sum_{j=1}^{z_i} \vec{r}_j^2 | G \rangle$, since we may replace $(\vec{H} \times \vec{r})^2 \rightarrow \frac{2}{3} \vec{H}^2 \vec{r}^2$. Thus, $\chi < 0 \Rightarrow$ diamagnetism

$$\chi = -\frac{N}{V} \frac{\partial^2 \Delta E_0}{\partial H^2} = -\frac{ne^2}{6mc^2} \langle G | \sum_{j=1}^{z_i} \vec{r}_j^2 | G \rangle$$

We define the mean square ionic radius, $\langle \vec{r}^2 \rangle \equiv \frac{1}{z_i} \langle \sum_{j=1}^{z_i} \vec{r}_j^2 \rangle_0$ in which case

$$\chi = -\frac{1}{6} z_i (na_B^3) \left(\frac{e^2}{\hbar c} \right)^2 \frac{\langle \vec{r}^2 \rangle}{a_B^2} \approx -10^{-5}$$

The molar susceptibility is

$$\chi^{\text{molar}} = \frac{N_A}{n} \chi = -7.9 \times 10^{-7} z_i \frac{\langle \vec{r}^2 \rangle}{a_B^2} \frac{\text{cm}^3}{\text{mol}}$$

Partially filled shells : van Vleck paramagnetism

First we consider $J=0$, corresponding to the case of one electron short of a half-filled shell.

(Atoms : C, Si, Cr, Ge, Mo, Sn, Sm, W, Pb, Pu). Then

$$\chi = \underbrace{-\frac{ne^2}{6mc^2} \langle G | \sum_{j=1}^{z_i} \vec{r}_j^2 | G \rangle}_{\text{Larmor diamagnetism}} + \underbrace{2n\mu_B \sum_n^{n \neq G} \frac{|\langle n | L^2 + 2S^2 | G \rangle|^2}{E_n - E_G}}_{\text{van Vleck paramagnetism}}$$

More generally, consider $J > 0$, which is the rule except for (i) filled shells, and (ii) one electron below half-filled. In this case the first term on the RHS

of $\Delta E_n(\vec{H})$ usually dominates. We then have the effective Hamiltonian within the J states:

$$H_{\text{eff}} = g_L \mu_B \vec{H} \cdot \vec{J} / \hbar$$

where g_L is the Landé g -factor,

$$g_L(J, L, S) = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

which comes from the Wigner-Eckart theorem, viz.

$$\langle JLSJ_2 | \vec{L} + 2\vec{S} | JLSJ_2' \rangle = g_L(JLS) \langle JLSJ_2 | \vec{J} | JLSJ_2' \rangle$$

The J manifold is $(2J+1)$ -fold degenerate when $\vec{H}=0$. At finite \vec{H} and T , compute the partition function,

$$Z = e^{-F/k_B T} = \sum_{j=-J}^J e^{-j\gamma H/k_B T} = \frac{\sinh((J+\frac{1}{2})\gamma H/k_B T)}{\sinh(\gamma H/2k_B T)}$$

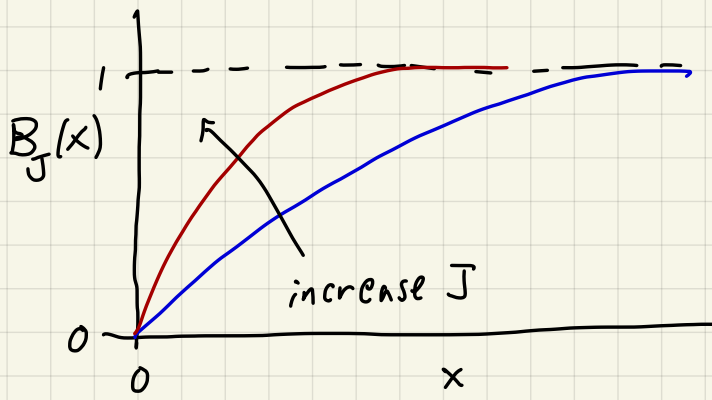
where $\gamma = g_L \mu_B$. The magnetization density is then

$$M = -\frac{N}{V} \frac{\partial F}{\partial H} = n \gamma J B_J(J \gamma H/k_B T)$$

where

$$B_J(x) = \left(1 + \frac{1}{2J}\right) \text{ctnh}\left[\left(1 + \frac{1}{2J}\right)x\right] - \frac{1}{2J} \text{ctnh}(x/2J)$$

is the Brillouin function.



Susceptibility:

$$\chi(H, T) = \frac{\partial M}{\partial H} = \frac{n J^2 \gamma^2}{k_B T} B'_J(J \gamma H / k_B T)$$

Set $H=0$:

$$\chi(H=0, T) = \frac{1}{3} (g_L \mu_B)^2 n \frac{J(J+1)}{k_B T}$$

which is Curie's law. Write $\chi(T) = n \mu_B^2 p^2 / 3 k_B T$
with $p = g_L \sqrt{J(J+1)}$.

Splitting by crystal fields:

• octahedral environment:

