Dept of Phys
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Diamagnetism and paramagnetism

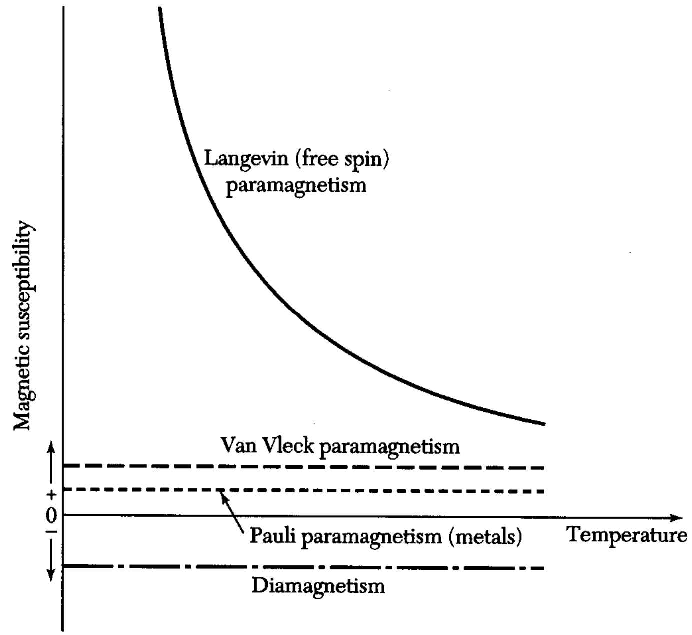
- Langevin diamagnetism
- paramagnetism
    - Hund's rules
    - Lande g-factor
    - Brillouin function
- crystal field splitting
    - quench of orbital angular momentum

atom

- nuclear demagnetization

- Pauli paramagnetism and Landau diamagnetism

free electron gas



Basics

- System energy $E(H)$ $\quad (E \to F = E - TS \text{ if } T \neq 0)$
- magnetization density $M(H) = -\frac{1}{V}\frac{\partial E}{\partial H}$
- susceptibility $\chi \equiv \frac{\partial M}{\partial H} = -\frac{1}{V}\frac{\partial^2 E}{\partial H^2}$

Atomic susceptibility

$$H = \sum_i \left(\frac{p_i^2}{2m} + V_i\right) + \mu_B\left(\vec{L} + g\vec{S}\right)\cdot\vec{H} + \frac{e^2}{2mc}\sum_i A_i^2, \quad \mu_B = \frac{e\hbar}{2mc}$$

$$= H_0 + \Delta H$$

Order of magnitude

- $$\mu_B\left(\vec{L} + g\vec{S}\right)\cdot\vec{H} \approx \mu_B H \approx \hbar\omega_c$$

  $$\approx 10^{-4} eV \quad \text{when } H = 1\,\text{T}$$

- $$\vec{A}_i = \frac{H}{2}(-y_i, x_i, 0)$$

  $$\frac{e^2}{2mc}\sum_i A_i^2 \approx \left(\frac{eH}{mc}\right)^2 ma_0^2, \quad a_0 \equiv \frac{\hbar^2}{me^2}$$

  $$\approx \frac{(\hbar\omega_c)^2}{e^2/a_0} \approx 10^{-5} \text{of the linear term at } H\text{=1 T}$$

Perturbation energy (to 2nd order)

$$\Delta E_n = \langle n|\Delta H|n\rangle + \sum_{n'\neq n} \frac{\left|\langle n|\Delta H|n'\rangle\right|^2}{E_n - E_{n'}}$$

$$= \mu_B \langle n|\vec{L} + g\vec{S}|n\rangle \cdot \vec{H} + \frac{e^2}{2mc^2}\langle n|\sum_i A_i^2|n\rangle + \sum_{n'}{}' \frac{\left|\langle n|\mu_B\left(\vec{L}+g\vec{S}\right)\cdot\vec{H}|n'\rangle\right|^2}{E_n - E_{n'}}$$

<u>Filled atomic shell</u>

(applies to noble gas, NaCl-like ions…etc)

Ground state $|0\rangle$:

$$\vec{L}|0\rangle = \vec{S}|0\rangle = 0$$

$$\therefore \quad \Delta E = \frac{e^2}{8mc^2} H^2 \langle 0|\frac{2}{3}\sum_i r_i^2|0\rangle \quad \text{(for spherical charge dist)}$$

For a collection of *N* ions,

$$\chi = -\frac{N}{V}\frac{\partial^2 \Delta E}{\partial H^2} = -\frac{e^2}{6mc^2}\frac{N}{V}\langle 0|\sum_i r_i^2|0\rangle < 0$$

Larmor (or Langevin) diamagnetism

Ground state of an atom with unfilled shell (no *H* field yet!):

- Atomic quantum numbers α, l, m_l, m_s
- Energy of an electron depends on α, l (no m_l, m_s)
- Degeneracy of electron level $\varepsilon_{\alpha,l}$: 2(2*l*+1)
- If an atom has *N* (non-interacting) valence electrons, then the degeneracy of the "atomic" ground state (with unfilled $\varepsilon_{\alpha,l}$ shell) is $C_N^{2(2l+1)}$

e-e interaction will lift this degeneracy partially, and then

- the atom energy is labeled by the conserved quantities *L and S*, each is (2L+1)(2S+1)-fold degenerate
- SO coupling would split these states further, which are labeled by J

What's the values of S, L, and J for the atomic ground state?

Use the Hund's rules (1925),

1. Choose the max value of S that is consistent with the exclusion principle
2. Choose the max value of L that is consistent with the exclusion principle and the 1st rule

To reduce Coulomb repulsion, electron spins like to be parallel, electron orbital motion likes to be in high *ml* state. Both helps disperse the charge distribution.

Example: 2 e's in the p-shell ($l_1 = l_2 = 1$, $s_1 = s_2 = 1/2$)

(a) (1,1/2)   (b) (0,1/2)   (c) (-1,1/2)

(a') (1,-1/2)   (b') (0,-1/2)   (c') (-1,-1/2)

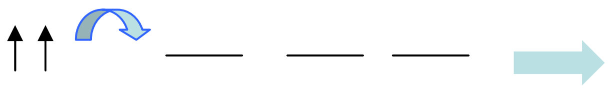
C^6_2 ways to put these 2 electrons in 6 slots

Spectroscopic notation:

$$^{2S+1}X_J \; (X = S, P, D\ldots)$$

$^1S_0, {}^3P_{0,1,2}, {}^1D_2$ are o.k.; $^3S, {}^1P, {}^3D$ are not.

(It's complicated. See Eisberg and Resnick App. K for more details)



$m_l =$ 1 0 -1

S=1

L=1

Ground state is $^3P_{0,1,2}$,

(2L+1)x(2S+1)=9-fold degenerate

Energy levels of Carbon atom

Configuration	Term	J	Level(cm^{-1})
$2s^22p^2$	^3P	0	0.00000
		1	16.41671
		2	43.41350
$2s^22p^2$	^1D	2	10192.66
$2s^22p^2$	^1S	0	21648.02

physics.nist.gov/PhysRefData/Handbook/Tables/carbontable5.htm

There is also the 3rd Hund's rule related to SO coupling (details below)

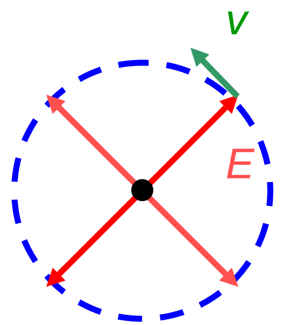
TABLE K-1. Possible Quantum Numbers for an np^2 Configuration

Entry	m_{l_1}	m_{s_1}	m_{l_2}	m_{s_2}	m_l'	m_s'	m_j'
1	+1	+1/2	+1	−1/2	+2	0	+2
2	+1	+1/2	0	+1/2	+1	+1	+2
3	+1	+1/2	0	−1/2	+1	0	+1
4	+1	+1/2	−1	+1/2	0	+1	+1
5	+1	+1/2	−1	−1/2	0	0	0
6	+1	−1/2	0	−1/2	+1	−1	0
7	+1	−1/2	−1	+1/2	0	0	0
8	+1	−1/2	−1	−1/2	0	−1	−1
9	0	+1/2	+1	−1/2	+1	0	+1
10	0	+1/2	0	−1/2	0	0	0
11	0	+1/2	−1	+1/2	−1	+1	0
12	0	+1/2	−1	−1/2	−1	0	−1
13	−1	+1/2	0	−1/2	−1	0	−1
14	−1	+1/2	−1	−1/2	−2	0	−2
15	−1	−1/2	0	−1/2	−1	−1	−2

Eisberg and Resnick
App. K

Setting $l_1 = l_2 = 1$, we find that the possible combinations of l', s', j', expressed in spectroscopic notation, are as follows: ${}^1S_0$, ${}^1P_1$, ${}^1D_2$, ${}^3S_1$, ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, ${}^3D_1$, ${}^3D_2$, ${}^3D_3$. The ${}^3D_3$ states are immediately ruled out because for these states there would be m_j' values of $+3$ and -3, but we see that there are none listed in Table K-1. Since there are no ${}^3D_3$ states, there can be no ${}^3D_2$ or ${}^3D_1$ states; all these states correspond to $\mathbf{S}'$ and $\mathbf{L}'$ vectors of the same magnitude in the same multiplet and they stand or fall together. Now, entry number 1 in the table says there must be states with $s' \geq 0$ and $l' \geq 2$, since $m_s' = -s', \ldots, s'$ and $m_l' = -l', \ldots, l'$. These requirements can be satisfied only by the states ${}^1D_2$. There are five such states corresponding to the five values $m_j' = -2, -1, 0, 1, 2$. Entry number 2 says that there must be states with $s' \geq 1$ and $l' \geq 1$. This requires the presence of the states ${}^3P_0$, ${}^3P_1$, ${}^3P_2$. For ${}^3P_0$ there is one state corresponding to $m_j' = 0$. For ${}^3P_1$ there are three states corresponding to $m_j' = -1, 0, 1$. For ${}^3P_2$ there are five corresponding to $m_j' = -2, -1, 0, 1, 2$. The number of states we have identified so far is $5 + 1 + 3 + 5 = 14$. Only a single state is left, and this must be a state with $m_j' = 0$ because all the other m_j' values of the table have been used. It is clear then that this must be the single quantum state ${}^1S_0$.

Review of SO coupling



An electron moving in a static E field feels an effective B field

$$\vec{B}_{eff} = \vec{E} \times \frac{\vec{v}}{c}$$

This B field couples with the electron spin

$$H_{SO} = -\vec{\mu} \cdot \vec{B}_{eff}$$

$$= -\left(\frac{q}{mc}\vec{S}\right) \cdot \left(\vec{E} \times \frac{\vec{v}}{c}\right), \quad \vec{E} = -\hat{r}\frac{d\phi}{dr} \text{ for central force}$$

$$= \left(\frac{q}{m^2c^2}\frac{d\phi}{rdr}\right)\vec{S} \cdot \vec{L}$$

(x 1/2 for Thomas precession, 1927)

$$\equiv \lambda \vec{S} \cdot \vec{L}$$

$\lambda > 0$ for less than half-filled (electron-like)
$\lambda < 0$ for more than half-filled (hole-like)

$$= \frac{\lambda}{2}\left(J^2 - L^2 - S^2\right)$$

Quantum states are now labeled by *L, S, J*

(2L+1)x(2S+1) degeneracy is further lifted to become (2J+1)-fold degeneracy

Hund's 3rd rule:

- if less than half-filled, then J=|L-S| has the lowest energy
- if more than half-filled, then J=L+S has the lowest energy

⇒ $^3P_0$ is the ground state in previous example

d-shell ($l = 2$)

n	$l_z = 2,$	$1,$	$0,$	$-1,$	-2	S	$L = \|\Sigma l_z\|$	J		SYMBOL
1	↓					1/2	2	3/2		${}^2D_{3/2}$
2	↓	↓				1	3	2	$J = \|L - S\|$	${}^3F_2$
3	↓	↓	↓			3/2	3	3/2		${}^4F_{3/2}$
4	↓	↓	↓	↓		2	2	0		${}^5D_0$
5	↓	↓	↓	↓	↓	5/2	0	5/2		${}^6S_{5/2}$
6	⇅	↑	↑	↑	↑	2	2	4		${}^5D_4$
7	⇅	⇅	↑	↑	↑	3/2	3	9/2	$J = L + S$	${}^4F_{9/2}$
8	⇅	⇅	⇅	↑	↑	1	3	4		${}^3F_4$
9	⇅	⇅	⇅	⇅	↑	1/2	2	5/2		${}^2D_{5/2}$
10	⇅	⇅	⇅	⇅	⇅	0	0	0		${}^1S_0$

f-shell ($l = 3$)

n	$l_z = 3,$	$2,$	$1,$	$0,$	$-1,$	$-2,$	-3	S	$L = \|\Sigma l_z\|$	J		
1	↓							1/2	3	5/2		${}^2F_{5/2}$
2	↓	↓						1	5	4		${}^3H_4$
3	↓	↓	↓					3/2	6	9/2		${}^4I_{9/2}$
4	↓	↓	↓	↓				2	6	4	$J = \|L - S\|$	${}^5I_4$
5	↓	↓	↓	↓	↓			5/2	5	5/2		${}^6H_{5/2}$
6	↓	↓	↓	↓	↓	↓		3	3	0		${}^7F_0$
7	↓	↓	↓	↓	↓	↓	↓	7/2	0	7/2		${}^8S_{7/2}$
8	⇅	↑	↑	↑	↑	↑	↑	3	3	6		${}^7F_6$
9	⇅	⇅	↑	↑	↑	↑	↑	5/2	5	15/2		${}^6H_{15/2}$
10	⇅	⇅	⇅	↑	↑	↑	↑	2	6	8		${}^5I_8$
11	⇅	⇅	⇅	⇅	↑	↑	↑	3/2	6	15/2	$J = L + S$	${}^4I_{15/2}$
12	⇅	⇅	⇅	⇅	⇅	↑	↑	1	5	6		${}^3H_6$
13	⇅	⇅	⇅	⇅	⇅	⇅	↑	1/2	3	7/2		${}^2F_{7/2}$
14	⇅	⇅	⇅	⇅	⇅	⇅	⇅	0	0	0		${}^1S_0$

[a]↑ = spin $\frac{1}{2}$; ↓ = spin $-\frac{1}{2}$.

Paramagnetism of an atom with unfilled shell

1) Ground state is nondegenerate (J=0)

$$\Delta E = \mu_B \langle 0 | \cancel{\vec{L} + g\vec{S}} | 0 \rangle \cdot \vec{H} + \frac{e^2}{2mc^2} \langle 0 | \sum_i A_i^2 | 0 \rangle + \sum_n{}' \frac{\left| \langle 0 | \mu_B \left(\vec{L} + g\vec{S} \right) \cdot \vec{H} | n \rangle \right|^2}{E_0 - E_n}$$

(A+M, Prob 31.4)

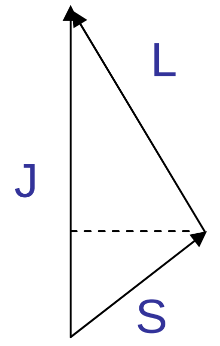
Van Vleck PM

2) Ground state is degenerate ($J \neq 0$)

Then the 1st order term almost always >> the 2nd order terms.

$$\vec{M} = -\mu_B \left(\vec{L} + 2\vec{S} \right) = -\mu_B \left(\vec{J} + \vec{S} \right)$$

Heuristic argument: J is fixed, L and S rotate around J, maintaining the triangle. So the magnetic moment is given by the component of L+2S parallel to J



$$\vec{S}_{//} = \frac{\vec{J} \cdot \vec{S}}{J^2} \vec{J} = \frac{\vec{J}}{2J^2} \left(J^2 - L^2 + S^2 \right)$$

$$= \frac{\vec{J}}{2J(J+1)} \left[J(J+1) - L(L+1) + S(S+1) \right]$$

$$\therefore \vec{M} = -g_J \mu_B \vec{J}$$

Lande g-factor (1921)

$$g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

$\Delta E(m_J) \sim H$, so $\chi = 0$?

No! these 2J+1 levels are closely packed (< kT), so $F(H)$ is nonlinear

Brillouin function

$$Z=\sum_{m_J=-J}^{J} e^{-E(m_J)/kT},\quad \Delta E(m_J)=g_J\mu_B m_J H\,(\sim 1K \text{ at } H=1\text{ T})$$

$$F=E-TS=-kT\ln Z$$

$$M=-\frac{N}{V}\frac{\partial F}{\partial H}=\frac{N}{V}g_J\mu_B J B_J\left(\frac{g_J\mu_B JH}{kT}\right)$$

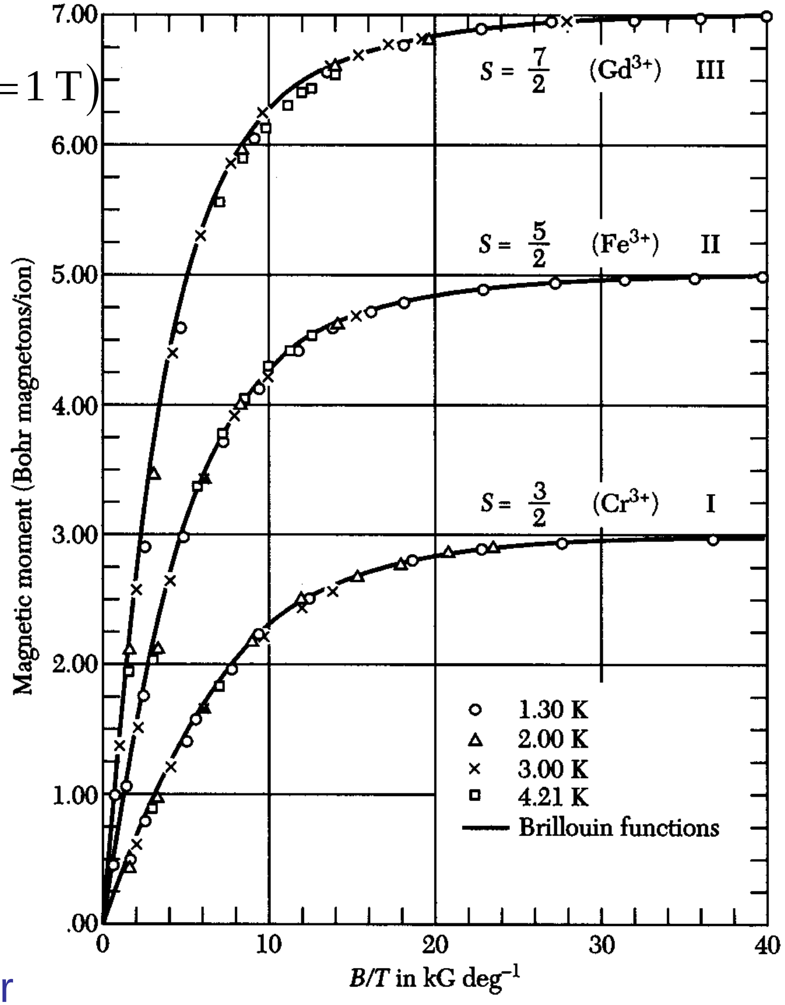
$$\text{where } B_J(x)\equiv\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right)-\frac{1}{2J}\coth\left(\frac{x}{2J}\right)$$

- $kT << g_J\mu_B JH \quad (x>>1)$

$$M=\frac{N}{V}g_J\mu_B J,\quad \chi=0$$

- $kT >> g_J\mu_B JH \quad (x<<1) \qquad B_J(x)\sim\frac{J+1}{3J}x$

$$M=\underbrace{\frac{N}{V}(g_J\mu_B)^2\frac{J(J+1)}{3kT}}_{\chi}H$$



- at room T, χ (para)$\sim$500 χ (dia) calculated earlier
- Curie's law $\chi=C/T$ (note: not good for J=0)

$$C=\frac{N}{V}\frac{(\mu_B p)^2}{3k},\quad \text{where } p=g_J\sqrt{J(J+1)}$$ (effective Bohr magneton number)

f-shell (rare earth ions)

In general (but not always)
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d …

ELEMENT (TRIPLY IONIZED)	BASIC ELECTRON CONFIGURATION	GROUND-STATE TERM	CALCULATED[b] p	MEASURED[c] p
La	$4f^0$	^1S	0.00	diamagnetic
Ce	$4f^1$	$^2F_{5/2}$	2.54	2.4
Pr	$4f^2$	$^3H_4$	3.58	3.5
Nd	$4f^3$	$^4I_{9/2}$	3.62	3.5
Pm	$4f^4$	$^5I_4$	2.68	—
Sm	$4f^5$	$^6H_{5/2}$	0.84	1.5
Eu	$4f^6$	$^7F_0$	0.00	3.4 $J=0$
Gd	$4f^7$	$^8S_{7/2}$	7.94	8.0
Tb	$4f^8$	$^7F_6$	9.72	9.5
Dy	$4f^9$	$^6H_{15/2}$	10.63	10.6
Ho	$4f^{10}$	$^5I_8$	10.60	10.4
Er	$4f^{11}$	$^4I_{15/2}$	9.59	9.5
Tm	$4f^{12}$	$^3H_6$	7.57	7.3
Yb	$4f^{13}$	$^2F_{7/2}$	4.54	4.5
Lu	$4f^{14}$	^1S	0.00	diamagnetic

Due to low-lying J-multiplets (see A+M, p.657)

Before ionization, La: $5p^6\ 6s^2\ 5d^1$; Ce: $5p^6\ 6s^2\ 4f^2$ …

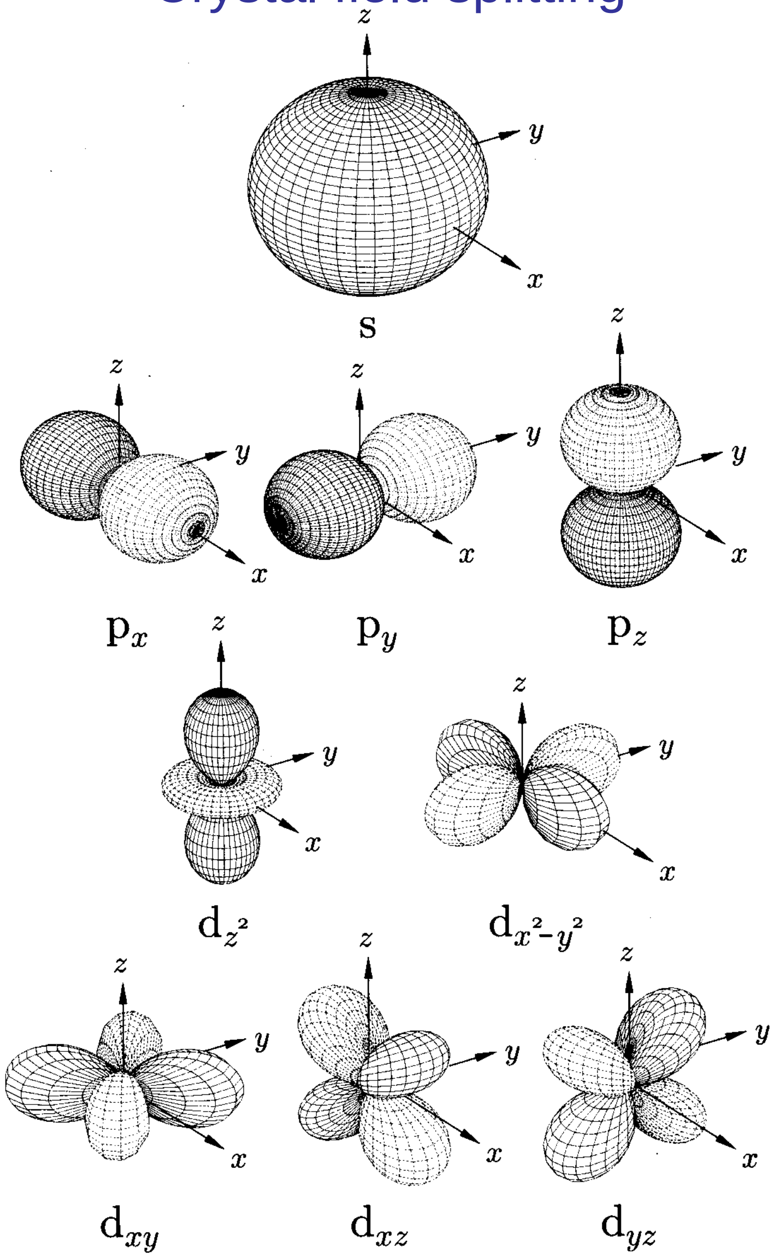
d-shell (iron group ions)

ELEMENT (AND IONIZATION)	BASIC ELECTRON CONFIGURATION	GROUND-STATE TERM	CALCULATED[b] p ($J = S$)	CALCULATED[b] p ($J = \|L \pm S\|$)	MEASURED[c] p
Ti^{3+}	$3d^1\ \cancel{4s^2}$	$^2D_{3/2}$	1.73	1.55	—
V^{4+}	$3d^1$	$^2D_{3/2}$	1.73	1.55	1.8
V^{3+}	$3d^2$	$^3F_2$	2.83	1.63	2.8
V^{2+}	$3d^3$	$^4F_{3/2}$	3.87	0.77	3.8
Cr^{3+}	$3d^3$	$^4F_{3/2}$	3.87	0.77	3.7
Mn^{4+}	$3d^3$	$^4F_{3/2}$	3.87	0.77	4.0
Cr^{2+}	$3d^4$	$^5D_0$	4.90	0	4.8
Mn^{3+}	$3d^4$	$^5D_0$	4.90	0	5.0
Mn^{2+}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{3+}	$3d^5$	$^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	$^5D_4$	4.90	6.70	5.4
Co^{2+}	$3d^7$	$^4F_{9/2}$	3.87	6.54	4.8
Ni^{2+}	$3d^8$	$^3F_4$	2.83	5.59	3.2
Cu^{2+}	$3d^9$	$^2D_{5/2}$	1.73	3.55	1.9

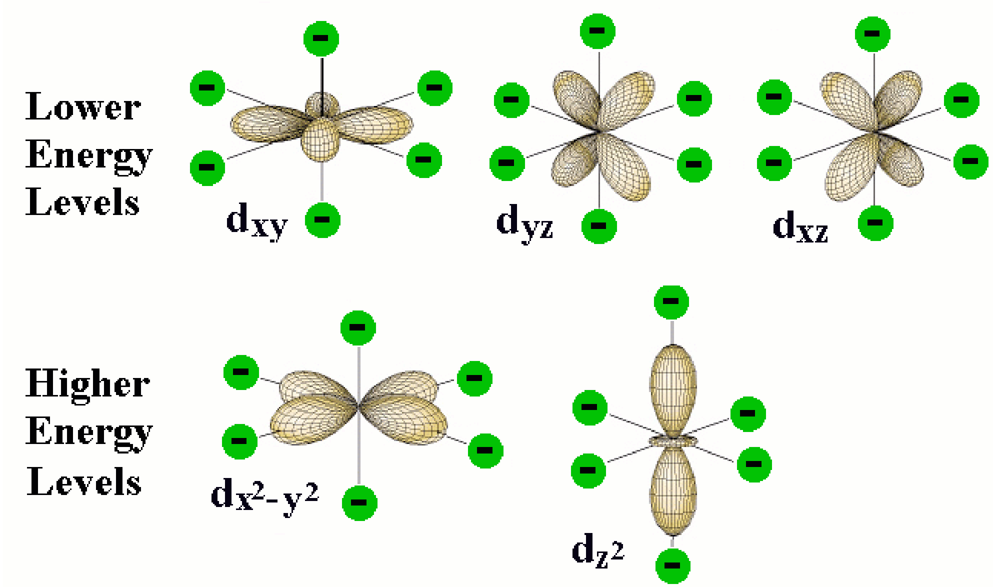
?

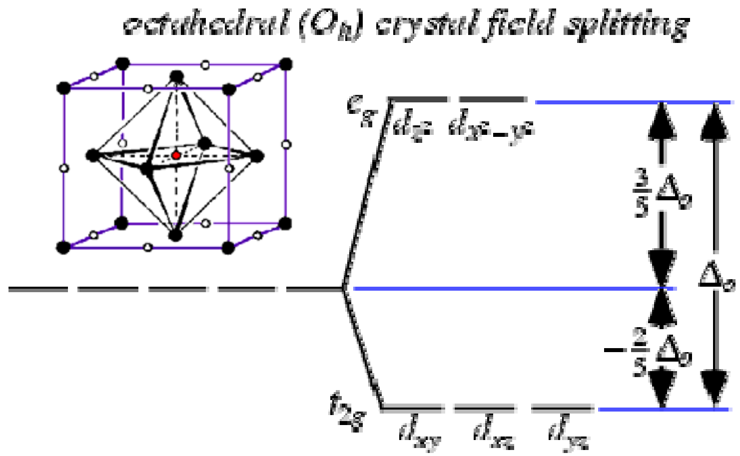
- Curie's law is still good, but p is mostly wrong
- Much better improvement if we let J=S

Crystal field splitting



In a crystal, crystal field may be more important than the LS coupling





Different symmetries would have different splitting patterns

Quench of orbital angular momentum

- Due to crystal field, energy levels are now labeled by L (not J)

- Orbital degeneracy not lifted by crystal field may be lifted by
1) LS coupling or 2) Jahn-Teller effect or both.

- The stationary state ϕ of a non-degenerate level can be chosen
to be real

$$\text{when } t \to -t,$$

$$\psi \to \psi^* (= c\psi \text{ if nondegenerate})$$

- $$\langle \psi | \vec{L} | \psi \rangle = \langle \psi | \vec{r} \times \frac{\hbar}{i} \nabla | \psi \rangle \text{ is purely imaginary}$$

$$\text{but } \langle \psi | \vec{L} | \psi \rangle \text{ has to be real also}$$

$$\therefore \langle \psi | \vec{L} | \psi \rangle = 0$$

$$\left(\langle \psi | L^2 | \psi \rangle \text{ can still be non-zero} \right)$$

- for 3d ions, crystal field > LS interaction

- for 4f ions, LS interaction > crystal field (because 4f is hidden inside
5p and 6s shells)

- for 4d and 5d ions that have stronger SO interaction, the 2 energies
maybe comparable and it’s more complicated.

- Langevin diamagnetism
- paramagnetism
    - Hund’s rules
    - Lande g-factor
    - Brillouin function
- crystal field splitting
    - quench of orbital angular momentum
- nuclear demagnetization
- Pauli paramagnetism and
Landau diamagnetism

Adiabatic demagnetization (proposed by Debye, 1926)

- The first way to reach below 1K

$$Z = \sum_{m_J=-J}^{J} e^{-E/kT}, \quad \text{assume } E \propto H$$

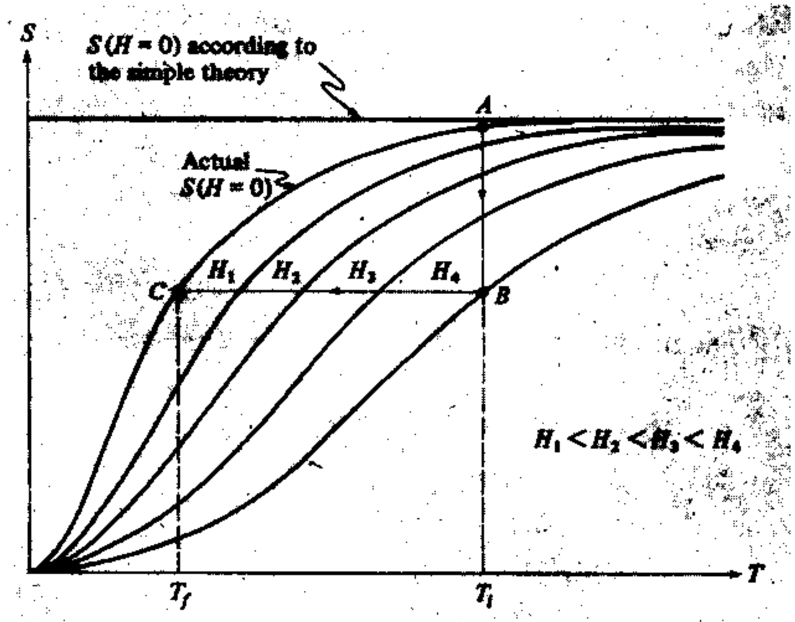
$$F = -kT \ln Z\left(\frac{H}{kT}\right)$$

$$S = -\frac{\partial F}{\partial T} = S\left(\frac{H}{kT}\right)$$

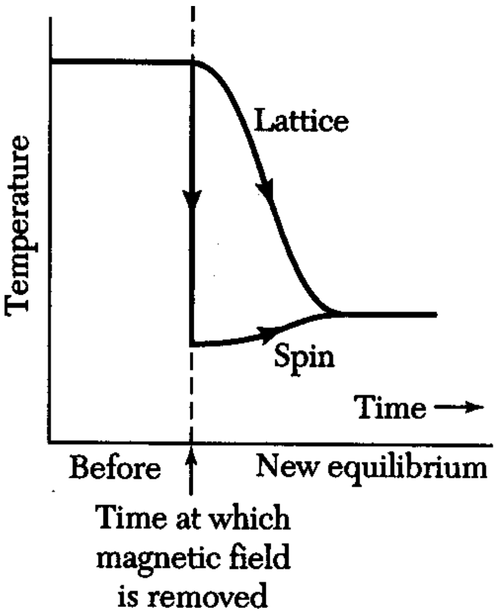
If S=constant, then $kT \sim H$ $\qquad T_f = T_i \dfrac{H_f}{H_i}$

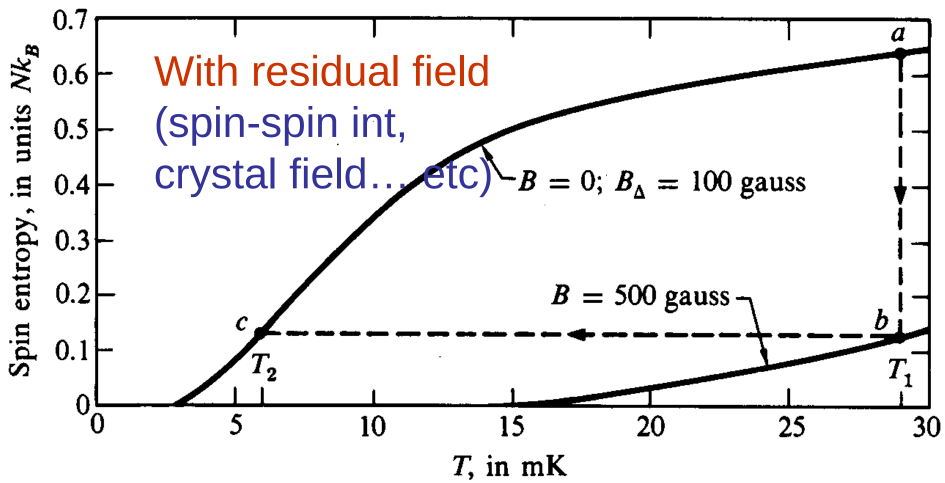
∴ We can reduce H to reduce T

Without residual field



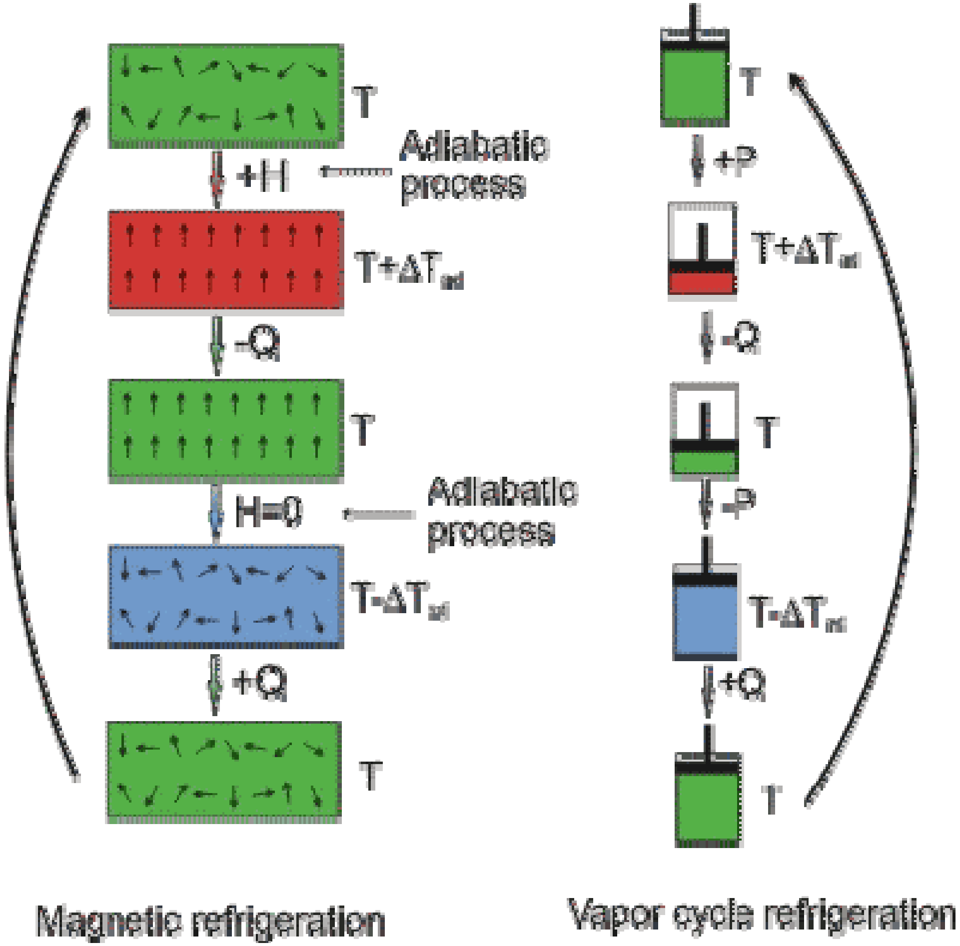
Freezing is effective only if spin specific heat is dominant (usually need $T \ll T_D$)

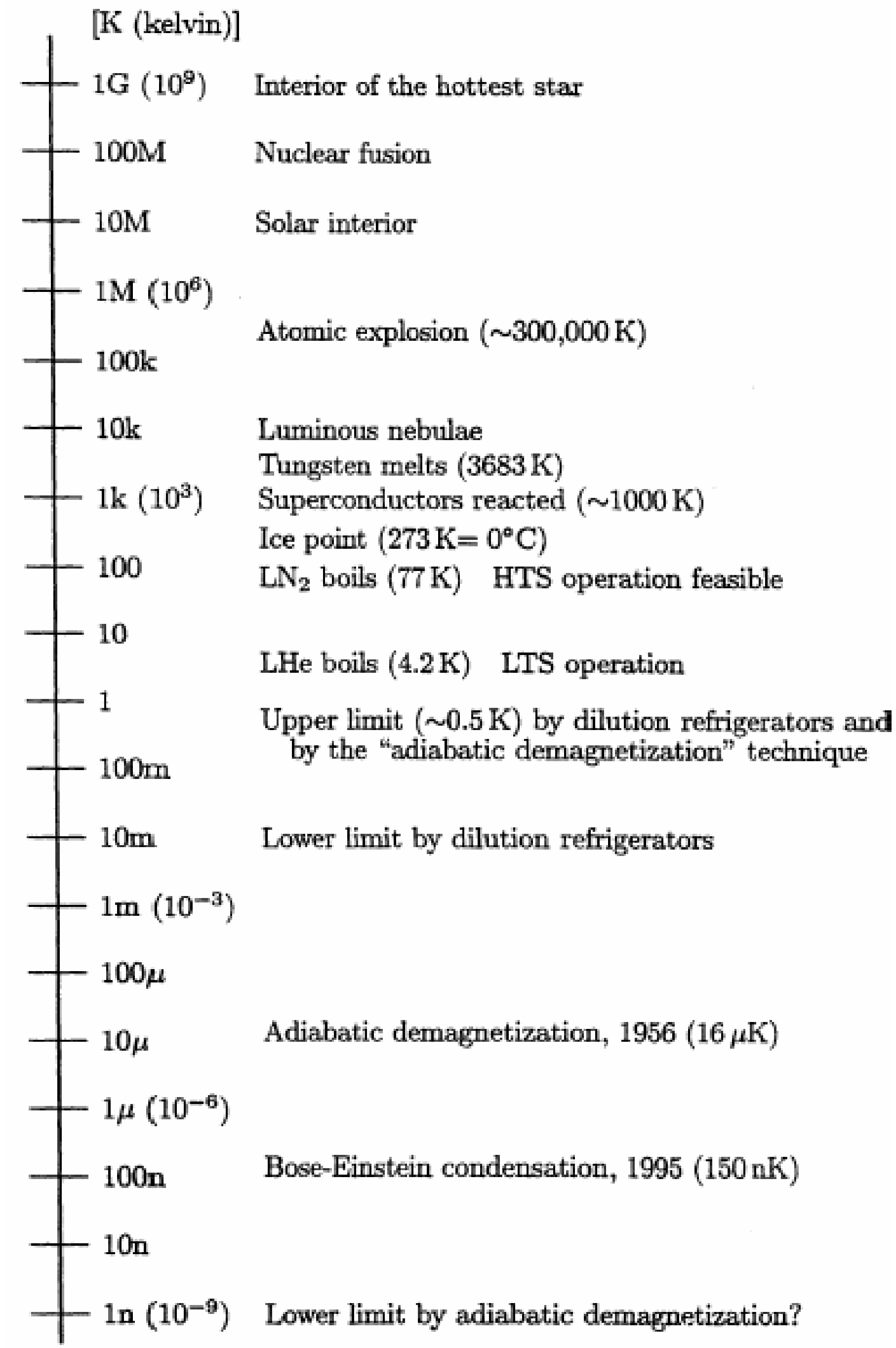




With residual field (spin-spin int, crystal field…, etc)

Can reach 10^{-6} K (dilution refrig only 10^{-3} K)


T
+H
Adiabatic process
T+ΔT
-Q
T
H=0
Adiabatic process
T-ΔT
+Q
T
T
+P
T+ΔT
-Q
T
-P
T-ΔT
+Q
T
Magnetic refrigeration
Vapor cycle refrigeration


[K (kelvin)]
1G (10^9) Interior of the hottest star
100M Nuclear fusion
10M Solar interior
1M (10^6)
Atomic explosion (~300,000 K)
100k
10k Luminous nebulae
Tungsten melts (3683 K)
1k (10^3) Superconductors reacted (~1000 K)
Ice point (273 K= 0°C)
100 LN2 boils (77 K) HTS operation feasible
10
LHe boils (4.2 K) LTS operation
1
Upper limit (~0.5 K) by dilution refrigerators and by the "adiabatic demagnetization" technique
100m
10m Lower limit by dilution refrigerators
1m (10^-3)
100μ
10μ Adiabatic demagnetization, 1956 (16 μK)
1μ (10^-6)
100n Bose-Einstein condensation, 1995 (150 nK)
10n
1n (10^-9) Lower limit by adiabatic demagnetization?

wikipedia

Pauli paramagnetism for free electron gas (1925)

- Orbital response to *H* neglected, consider only spin response
- One of the earliest application of the exclusion principle

$$N = N_\uparrow + N_\downarrow$$

$$M = \frac{1}{V}\left(N_\uparrow - N_\downarrow\right)\mu_B$$

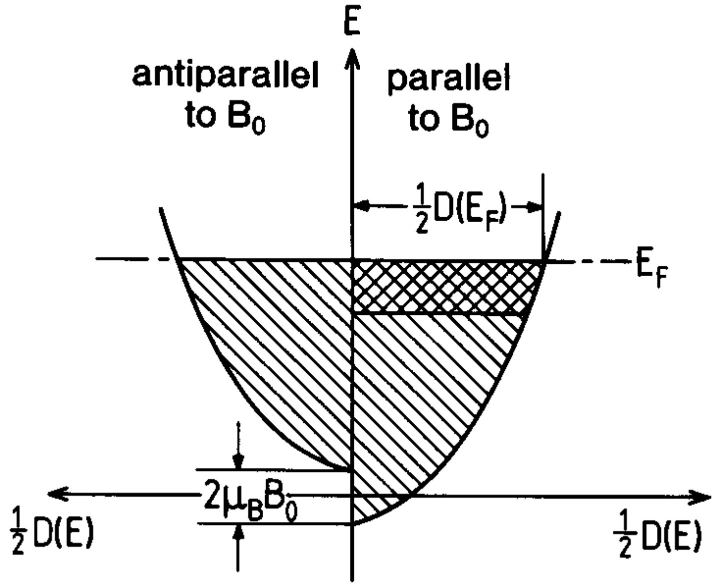
For $T << T_F$,

$$n_\uparrow - n_0 \cong \frac{g(\varepsilon_F)}{2}\mu_B H;$$

$$n_\downarrow - n_0 \cong -\frac{g(\varepsilon_F)}{2}\mu_B H.$$

$$\therefore M = g(\varepsilon_F)\mu_B^2 H$$

$$\Rightarrow \quad \chi_{Pauli} = g(\varepsilon_F)\mu_B^2 \sim 10^{-6}$$



Landau diamagnetism (1930)

- The orbital response neglected earlier gives slight DM
- The calculation is not trivial

$$\chi_{Landau} = -\frac{e^2 k_F}{12\pi^2 mc^2}$$

$$= -\frac{1}{3}\chi_{Pauli}$$