PHY331
Magnetism

Lecture 5

Last week

- We calculated paramagnetic susceptibility using an entirely classical approach and obtained Curie's Law for a paramagnet.

$$\chi = \frac{M}{H} = \frac{\mu_0 N m^2}{3kT} = \frac{C}{T}$$

- We saw that quantization of angular momentum (*l*) and spin (*s*) will be important components of a quantum theory of paramagnetism.

This week

We will first learn how to calculate the magnetic dipole moment of an atom.

This requires knowledge of some atomic physics, and uses Hund's rules (rules to work out the relative ordering of electronic spins).

Will compare calculated values with measured data.

Russell- Saunders coupling

- Need to add the spin and angular momentum of all electrons in an atom.

$$\underline{L} = \sum_i \underline{l}_i \qquad \underline{S} = \sum_i \underline{s}_i$$

- L and S combine to give the total angular momentum J for the atom where,

total AM = orbital AM + spin AM

$$\underline{J} = \underline{L} \pm \underline{S}$$

There are rules how we do this addition. These rules are called Hund's rules.

Hund's rules

1. Full shells and subshells do not contribute to total S , and L quantum numbers.

2. The term with maximum S (termed multiplicity) has the lowest energy level.

3. For a given S, the term with the largest value of L has the lowest energy.

4. For atoms with shells less than half-full:

$$\underline{J} = \left| \underline{L} - \underline{S} \right|$$

For atoms with shell more than half-full:

$$\underline{J} = \underline{L} + \underline{S}$$

For atoms with shell just half full, then 1. (above) gives $\underline{L} = 0$, so

$$\underline{J} = \underline{S}$$

Hund Rules

- An atom will always attempt to reach its lowest energy configuration. The Hund rules provide a way of determining which energetic configuration is the lowest. In general, a greater total spin state usually makes the resulting atom more stable, most commonly manifested in a lower energy state, because it forces the unpaired electrons to reside in different spatial orbitals.

- **Rule 1 – maximum spin multiplicity.** Electrons in singly occupied orbitals are less effectively screened or shielded from the nucleus, so that such orbitals contract and electron nuclear attraction energy becomes greater in magnitude.

- **Rule 2 – maximum orbital angular momentum** This rule deals again with reducing the repulsion between electrons. It can be understood from the classical picture that if all electrons are orbiting in the same direction (higher orbital angular momentum) they meet less often than if some of them orbit in opposite directions. When electrons 'meet' (interact) the Coulombic repulsive force increases, which separates them. This separation adds potential energy, thereby increasing their energy level.

So how do we calculate the magnetic dipole moment of an atom?

Both the **orbital motion** and the **spin** of the electron produce a magnetic dipole moment **but,** the electron spin *creates twice as much moment*!

Remember that,
$$\underline{m} = -\frac{\underline{L}}{2m} q$$

So for the orbital motion,
$$\underline{m}_L = -\frac{e\hbar}{2m} \sqrt{L(L+1)}$$

(recall magnitude of AM = $\hbar\sqrt{l(l+1)}$)

But
$$\underline{m}_s = -2\frac{e\hbar}{2m} \sqrt{S(S+1)}$$

(recall magnitude of spin AM = $\hbar\sqrt{s(s+1)}$)

The quantity $\dfrac{e\hbar}{2m}$ is known as the *Bohr magneton* it is the fundamental unit of magnetic dipole moment. It is given the symbol μ_B, its value is 9.274×10^{-24} A m^2

- From now on we will **adopt the symbol μ** for magnetic dipole moment (in place of $\underline{m}$) so that,

Orbital magnetic moment

$$\mu_L = -\sqrt{L(L+1)}\ \mu_B$$

Spin magnetic moment

$$\mu_S = -2\sqrt{S(S+1)}\ \mu_B$$

Vector diagram of μ_J, μ_L, μ_S

The resultant magnetic dipole moment $\underline{\mu_R}$ ***does not*** lie along the resultant $\underline{J}$, - it precesses around $\underline{J}$. *However, it is* the ***component*** of μ_R which lies ***parallel*** to $\underline{J}$ that gives the ***actual value*** of the magnetic dipole moment, since the perpendicular component (µ') ***averages to zero.*** The magnitude of this is, a new parameter g is obtained by applying the cosine rule to the vector triangles shown in the figure.
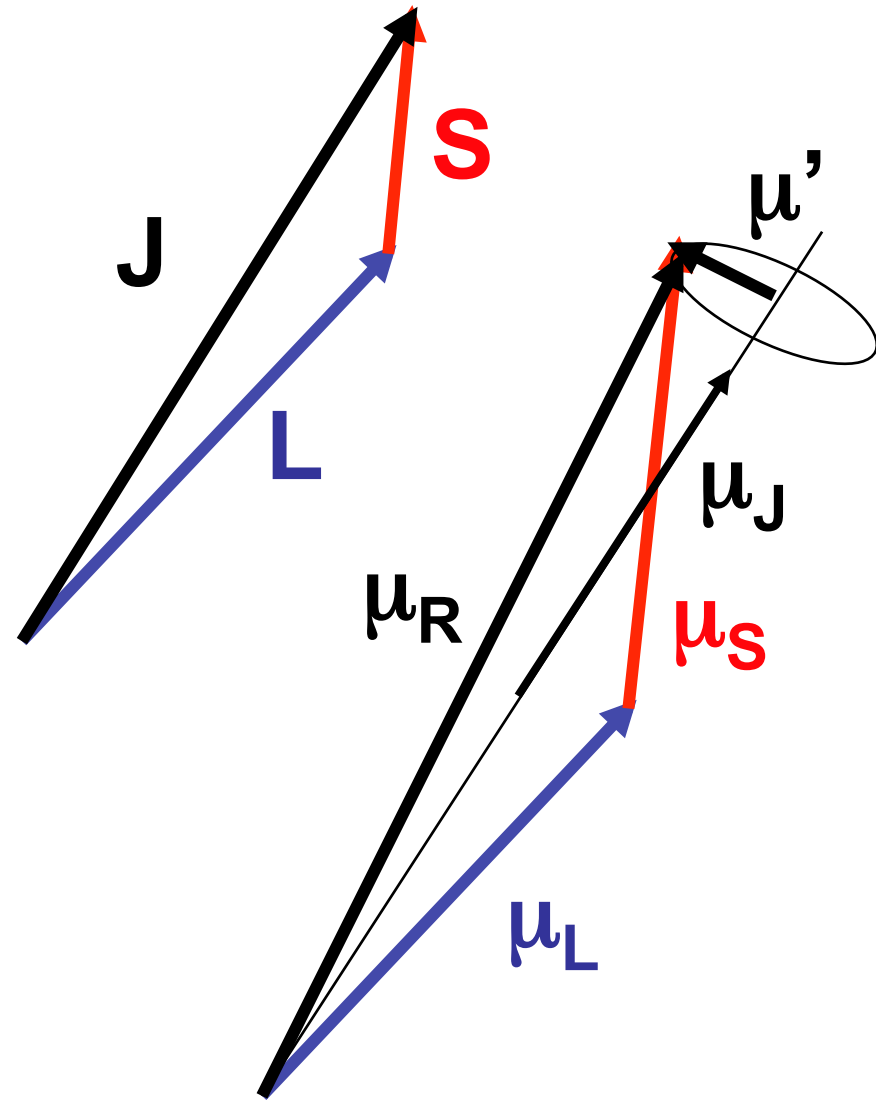
$$\mu_J = g\sqrt{J(J+1)}\,\mu_B$$

"g" is called the "Landé splitting factor" and is given by,

$$g = \left\{ \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \right\}$$

It obviously compensates for the different contributions from the orbital motion and the electron spin, since substitution shows that,

$$g = 1 \quad \text{when} \quad S = 0$$

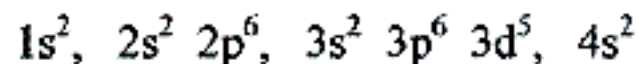(i.e. in an atom with no electron spin contribution)

$$\text{and,} \quad g = 2 \quad \text{when} \quad L = 0$$

(i.e. an atom where no AM contribution and all contribution to J comes from electron spin)
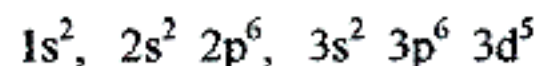
Calculation of magnetic moment values

(i) the manganese Mn^{2+} ion

the electronic configuration of Mn is $1s^2,\ 2s^2\ 2p^6,\ 3s^2\ 3p^6\ 3d^5,\ 4s^2$

so that Mn^{2+} will be $1s^2,\ 2s^2\ 2p^6,\ 3s^2\ 3p^6\ 3d^5$.

the values of l for these shells are,

shell	s	p	d	f
l	0	1	2	3

there are 10 3d states in all $i.e..3d^{10}$

l	2	2	2	2	2
m_l	2	1	0	-1	-2
s	½	½	½	½	½

and

l	2	2	2	2	2
m_l	2	1	0	-1	-2
s	-½	-½	-½	-½	-½

Apply Hund's Rules

Step 1: Add electron spins to give maximum value of S (rule 2)

$$S = (5 \times 1/2) = 5/2$$

Step 2: Add orbital momenta to give maximum L (rule 3)

L = -2 + -1 + 0 + 1 + 2 = 0

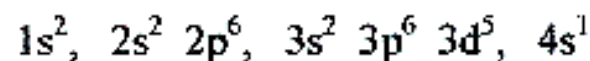Step 3, As shell is half filled, we have L=0 so J = S = 5/2

$$g = \left(\frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \right) = \left(\frac{3}{2} + \left\{ \frac{\frac{5}{2} \cdot \frac{7}{2} - 0}{2\frac{5}{2} \cdot \frac{7}{2}} \right\} \right) = 2$$
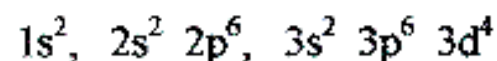
This is as expected for 'spin-only' atom, and so

$$\mu_J = g\sqrt{J(J+1)}\mu_B = 2\sqrt{\frac{5}{2} \cdot \frac{7}{2}}\mu_B = 5.92\mu_B$$

(ii) the chromium Cr^{2+} ion

the electronic configuration of Cr is $1s^2,\ 2s^2\ 2p^6,\ 3s^2\ 3p^6\ 3d^5,\ 4s^1$

        so that Cr^{2+} will be $1s^2,\ 2s^2\ 2p^6,\ 3s^2\ 3p^6\ 3d^4$

the values of l for these shells are,

shell	s	p	d	f
l	0	1	2	3

there are 10 3d states in all   *i.e.* $3d^{10}$

l	2	2	2	2	2
m_l	2	1	0	-1	-2
s	½	½	½	½	½

and

l	2	2	2	2	2
m_l	2	1	0	-1	-2
s	-½	-½	-½	-½	-½

Apply Hund's Rules

Step 1: Add electron spins to give maximum value of S (rule 2)

$$S = (4 \times 1/2) = 2$$

Step 2: Add orbital momenta to give maximum L (rule 3)

L = -1 + 0 + 1 + 2 = 2

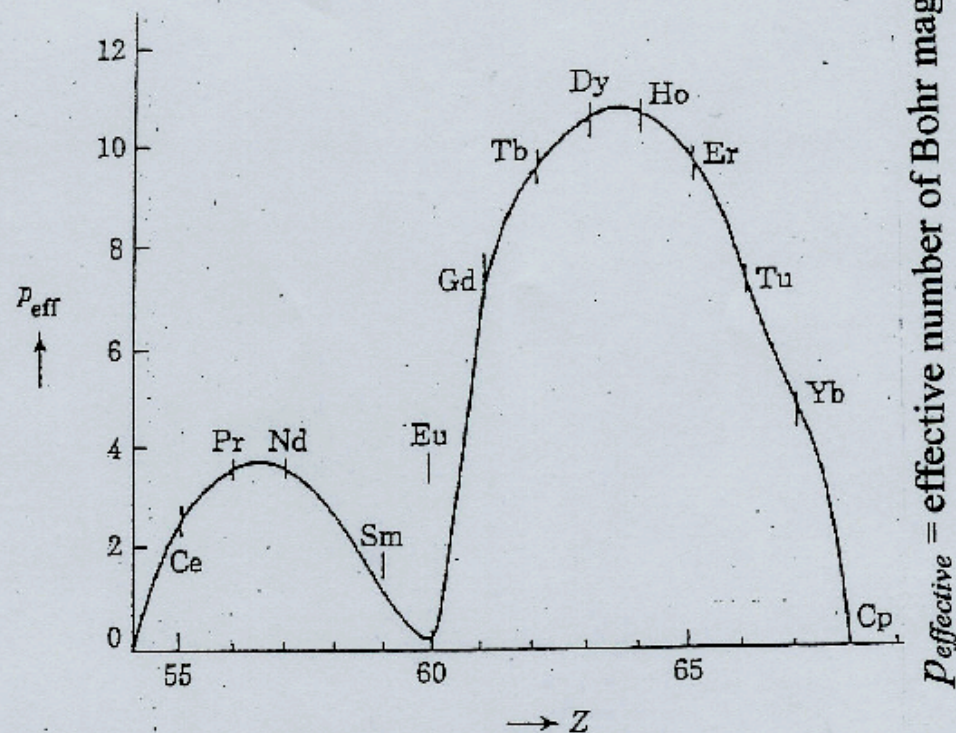Step 3, J = L ± S. As shell is less than half filled, we must have

J = L - S,   Thus J = 2 - 2 = 0

$$\mu_J = g\sqrt{J(J+1)}\mu_B = 0$$
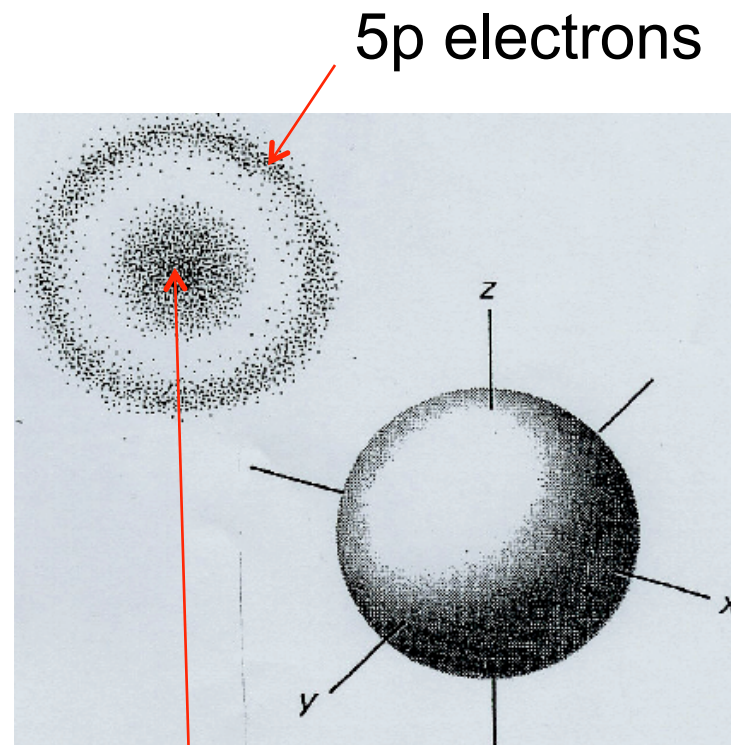
(not very exciting!! - don't need to calculate g)

How does this work in practice?

ii) paramagnetic salts containing
Rare Earth ions

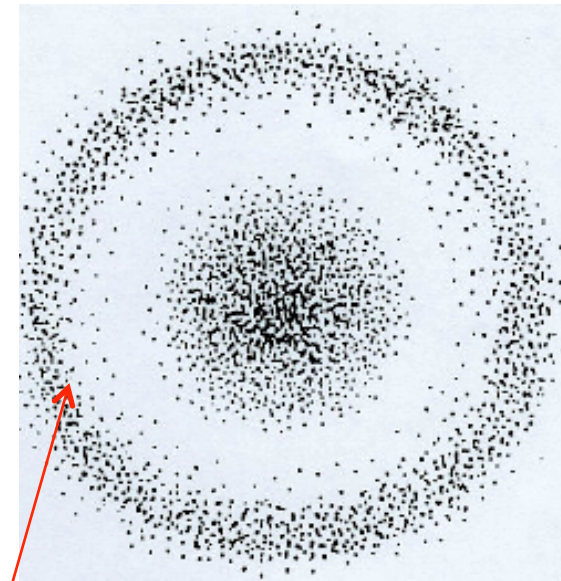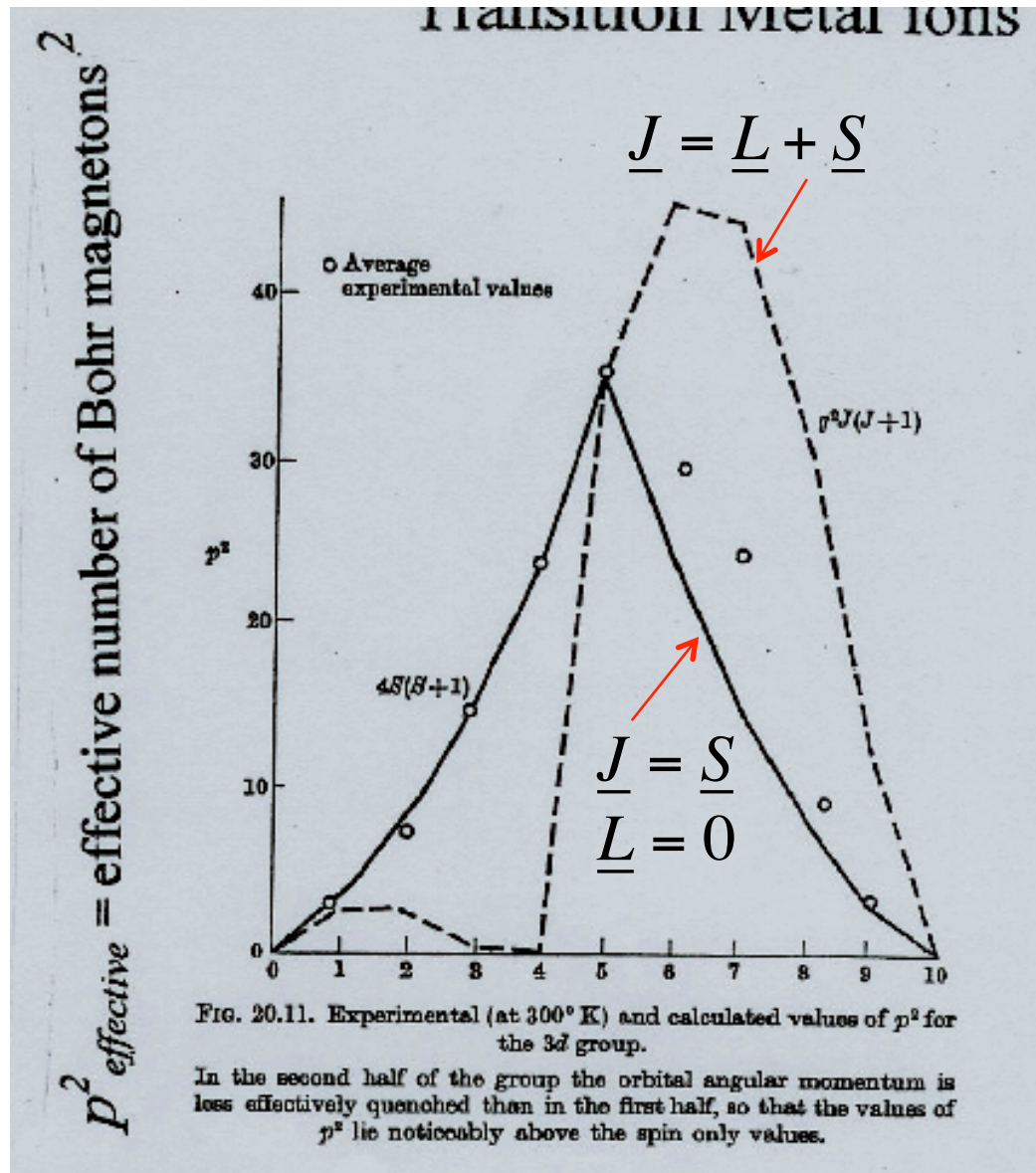$P_{effective}$ = effective number of Bohr magnetons

The effective moment in Bohr magnetons as function of the number of electrons for the trivalent positive rare earth ions

$$\mu_{eff} = p_{eff}\, \mu_B$$

5p electrons

Magnetic 4f electrons are well inside electron cloud. screened from internal crystal fields.

Transition metal ions

$$\underline{J} = \underline{L} + \underline{S}$$

$p^2 J(J+1)$

o Average
experimental values

$4S(S+1)$

$$\underline{J} = \underline{S}$$
$$\underline{L} = 0$$

p^2

FIG. 20.11. Experimental (at 300° K) and calculated values of p^2 for the 3d group.

In the second half of the group the orbital angular momentum is less effectively quenched than in the first half, so that the values of p^2 lie noticeably above the spin only values.

p^2 _effective_ = effective number of Bohr magnetons^2

'Magnetic electrons are now 3d
Electrons which are outer
electrons of the transition metals.
Fully exposed to internal crystalline
fields. Orbital motion cannot
contribute to magnetic moment -
determined by electron spin alone

Quenching of the orbital motion.

$$\mu_{eff} = p_{eff}\,\mu_B$$

Summary

Learned how to calculate the magnetic dipole moment of an atom.

Introduced the "Landé splitting factor" g. Saw that it compensates for the different contributions from the orbital motion and the electron spin.

Compare calculated values with measured data