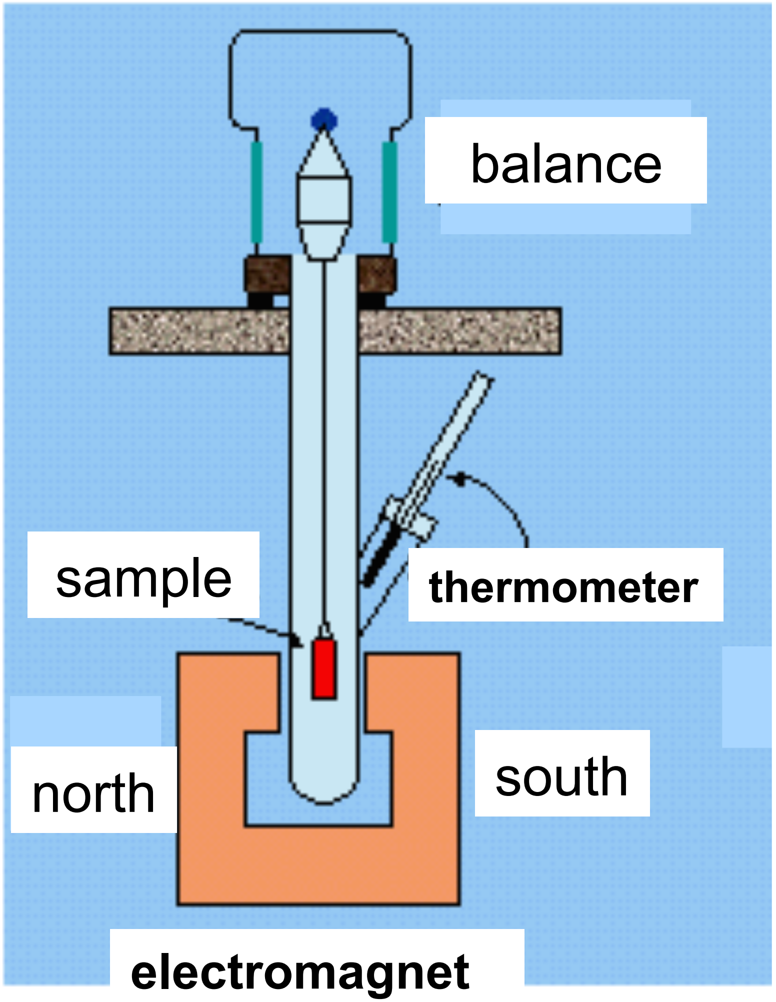
Lecture 19: Magnetic properties and the Nephelauxetic effect



left: the Gouy balance for determining the magnetic susceptibility of materials

Magnetic properties

Magnetic susceptibility (μ) and the spin-only formula.

Materials that are diamagnetic are repelled by a magnetic field, whereas paramagnetic substances are attracted into a magnetic field, i.e. show magnetic susceptibility. The spinning of unpaired electrons in paramagnetic complexes of d-block metal ions creates a magnetic field, and these spinning electrons are in effect small magnets. The magnetic susceptibility, μ, due to the spinning of the electrons is given by the spin-only formula:

$$\boxed{\mu(\text{spin-only}) = \sqrt{n(n+2)}}$$

Where n = number of unpaired electrons.

Magnetic properties

The spin-only formula applies reasonably well to metal ions from the first row of transition metals: (units = μ_{B}, Bohr-magnetons)

Metal ion	d^n configuration	μ_{eff}(spin only)	μ_{eff} (observed)
Ca^{2+}, Sc^{3+}	d^0	0	0
Ti^{3+}	d^1	1.73	1.7-1.8
V^{3+}	d^2	2.83	2.8-3.1
V^{2+}, Cr^{3+}	d^3	3.87	3.7-3.9
Cr^{2+}, Mn^{3+}	d^4	4.90	4.8-4.9
Mn^{2+}, Fe^{3+}	d^5	5.92	5.7-6.0
Fe^{2+}, Co^{3+}	d^6	4.90	5.0-5.6
Co^{2+}	d^7	3.87	4.3-5.2
Ni^{2+}	d^8	2.83	2.9-3.9
Cu^{2+}	d^9	1.73	1.9-2.1
Zn^{2+}, Ga^{3+}	d^{10}	0	0

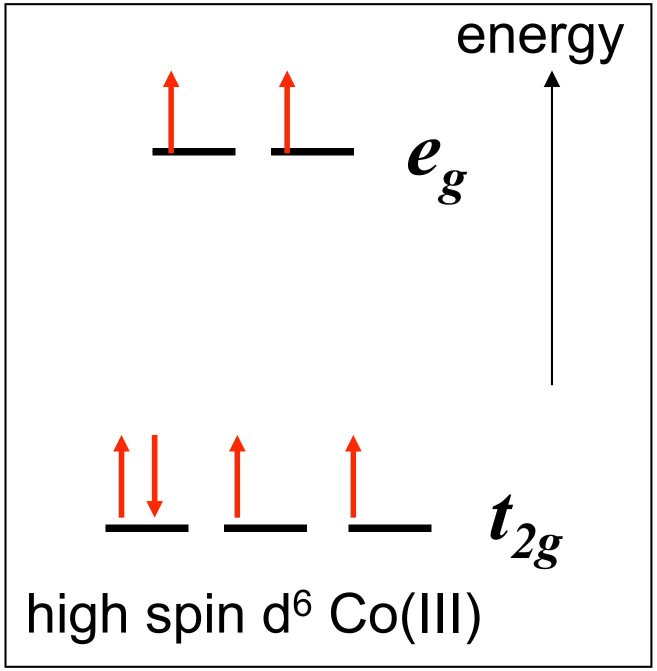
Example:

What is the magnetic susceptibility of $[CoF_6]^{3-}$, assuming that the spin-only formula will apply:

$[CoF_6]^{3-}$ is high spin Co(III). (you should know this). High-spin Co(III) is d^6 with four unpaired electrons, so $n = 4$.

We have $\mu eff = \sqrt{n(n+2)}$

$$\boxed{= 4.90\ \mu_B}$$

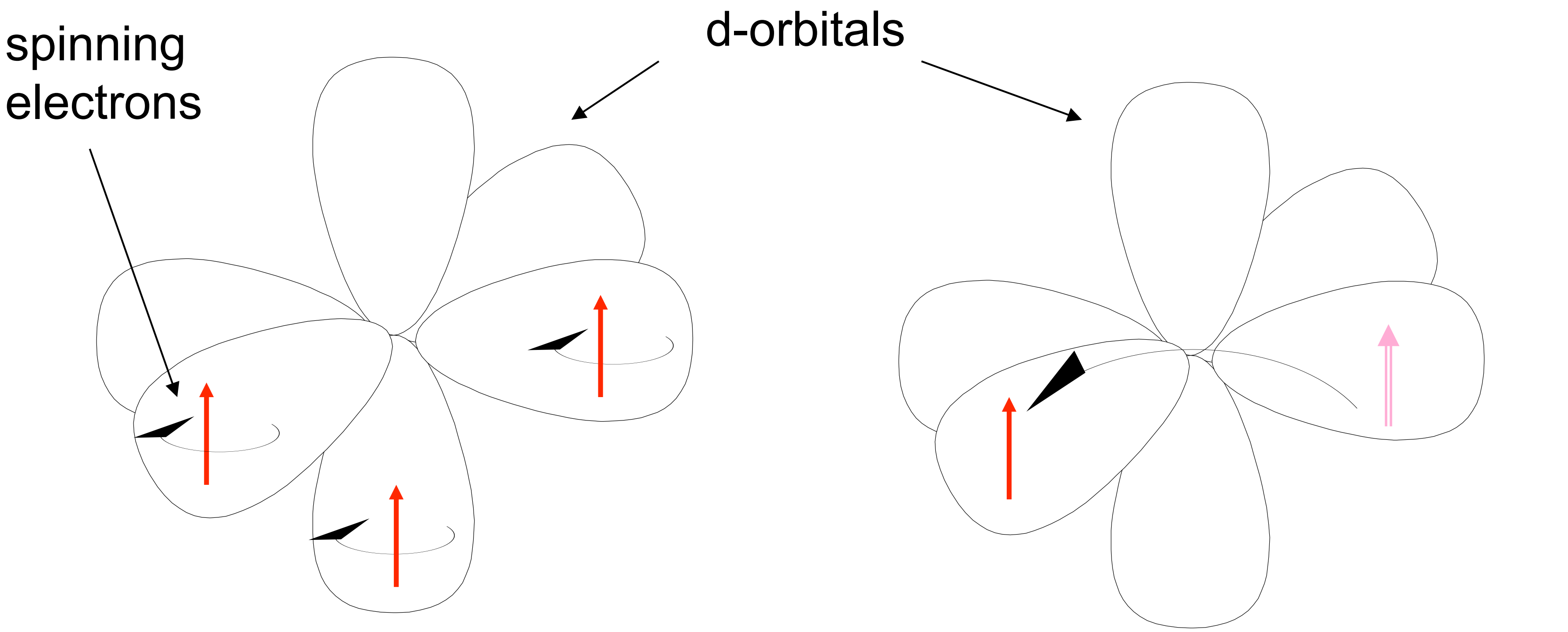


Spin and Orbital contributions to Magnetic susceptibility

For the first-row d-block metal ions the main contribution to magnetic susceptibility is from electron spin. However, there is also an orbital contribution from the motion of unpaired electrons from one d-orbital to another. This motion constitutes an electric current, and so creates a magnetic field (see next slide). The extent to which the orbital contribution adds to the overall magnetic moment is controlled by the spin-orbit coupling constant, λ. The overall value of μ_{eff} is related to μ(spin-only) by:

$$\boxed{\mu_{eff} \quad = \quad \mu(\text{spin-only})(1 - \alpha\lambda/\Delta_{oct})}$$

Diagrammatic representation of spin and orbital contributions to μ_{eff}



spin contribution – electrons are spinning creating an electric current and hence a magnetic field

orbital contribution - electrons move from one orbital to another creating a current and hence a magnetic field

Spin and Orbital contributions to Magnetic susceptibility

$$\mu_{eff} = \mu(\text{spin-only})(1 - \alpha\lambda/\Delta_{oct})$$

In the above equation, λ is the spin-orbit coupling constant, and α is a constant that depends on the ground term: For an A ground state, $\alpha = 4$. and for an E ground state, $\alpha = 2$. Δ_{oct} is the CF splitting. Some values of λ are:

	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
λ, cm^{-1}	155	105	90	88	-102	-177	-315	-830

Spin and Orbital contributions to Magnetic susceptibility

Example: Given that the value of the spin-orbit coupling constant λ, is -316 cm^{-1} for Ni^{2+}, and Δ_{oct} is 8500 cm^{-1}, calculate μ_{eff} for $[Ni(H_2O)_6]^{2+}$. (Note: for an A ground state α = 4, and for an E ground state α = 2).

High-spin Ni^{2+} = d^8 = **A** ground state, so α = 4.

n = 2, so $\mu(\text{spin only}) = (2(2+2))^{0.5} = 2.83\ \mu_B$

$$\mu_{eff} = \mu(\text{spin only})(1 - (-316\ cm^{-1} \times (4/8500\ cm^{-1})))$$

$$= 2.83\ \mu_B \times 1.149$$

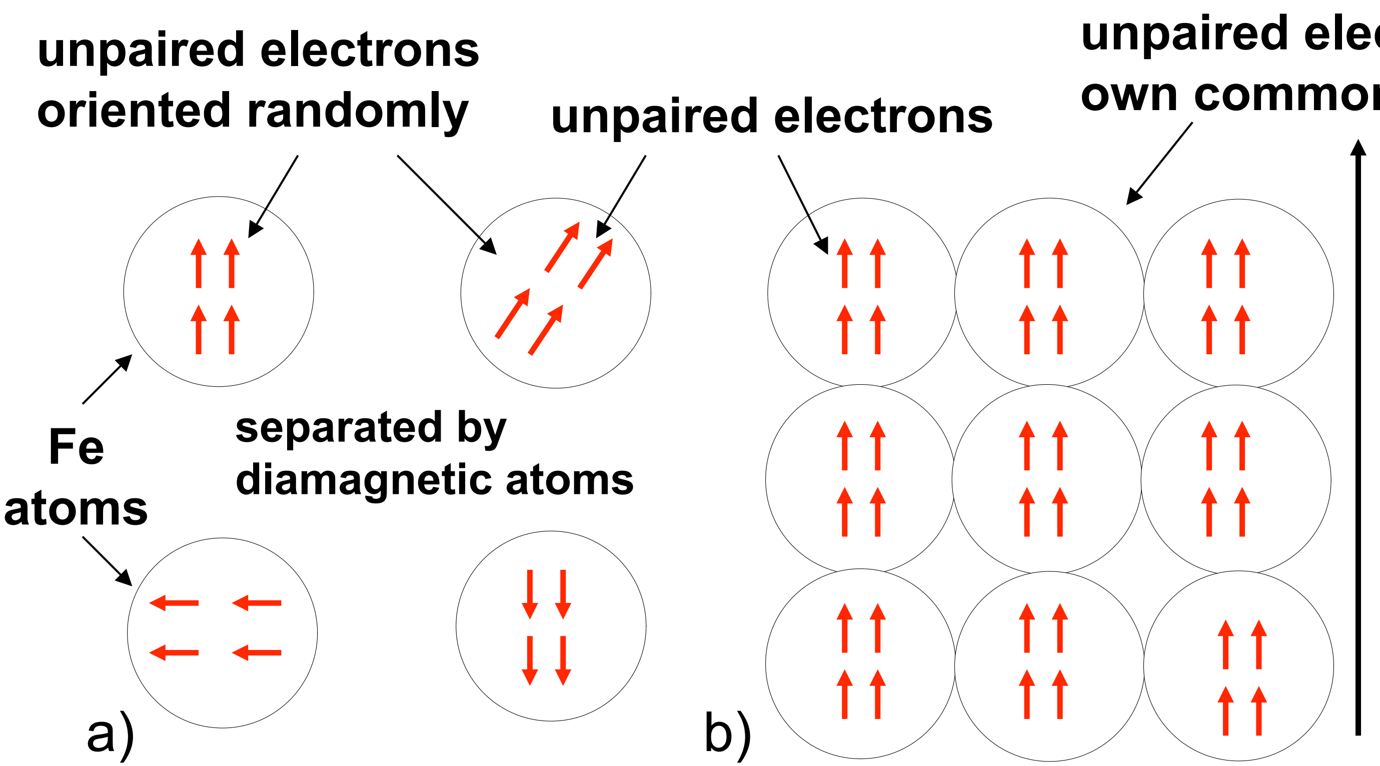
$$\boxed{= 3.25\ \mu_B}$$

Spin and Orbital contributions to Magnetic susceptibility

The value of λ is negligible for very light atoms, but increases with increasing atomic weight, so that for heavier d-block elements, and for f-block elements, the orbital contribution is considerable. For 2nd and 3rd row d-block elements, λ is an order of magnitude larger than for the first-row analogues. Most 2nd and 3rd row d-block elements are low-spin and therefore are diamagnetic or have only one or two unpaired electrons, but even so, the value of μ_{eff} is much lower than expected from the spin-only formula. (Note: the only high-spin complex from the 2nd and 3rd row d-block elements is $[PdF_6]^{4-}$ and PdF_2).

Ferromagnetism:

In a normal paramagnetic material, the atoms containing the unpaired electrons are magnetically dilute, and so the unpaired electrons in one atom are not aligned with those in other atoms. However, in ferromagnetic materials, such as metallic iron, or iron oxides such as magnetite (Fe_3O_4), where the paramagnetic iron atoms are very close together, they can create an internal magnetic field strong enough that all the centers remain aligned:

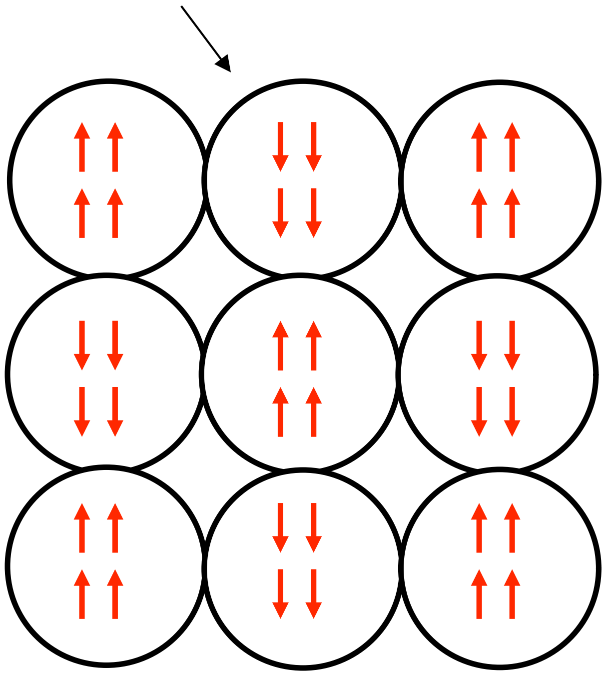


a) paramagnetic, magnetically dilute in e.g. $[Fe(H_2O)_6]Cl_2$.

b) **ferromagnetic**, as in metallic Fe or some Fe oxides.

Antiferromagnetism:

electron spins in opposite directions in alternate metal atoms



antiferromagnetism

Here the spins on the unpaired electrons become aligned in opposite directions so that the μ_{eff} approaches zero, in contrast to ferromagnetism, where μ_{eff} becomes very large. An example of anti-ferromagnetism is found in MnO.