

where \mathbf{A} is the magnetic vector potential. We choose a gauge¹ such that

$$\mathbf{A}(\mathbf{r}) = \frac{\mathbf{B} \times \mathbf{r}}{2}. \quad (2.5)$$

Then the kinetic energy must be altered according to the prescription described in Section 1.2. Since the charge on the electron is $-e$, the kinetic energy is $[\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i)]^2/2m_e$ and hence the perturbed Hamiltonian must now be written

$$\hat{\mathcal{H}} = \sum_{i=1}^Z \left(\frac{[\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i)]^2}{2m_e} + V_i \right) + g\mu_B \mathbf{B} \cdot \mathbf{S} \quad (2.6)$$

$$= \sum_i \left(\frac{p_i^2}{2m_e} + V_i \right) + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_i (\mathbf{B} \times \mathbf{r}_i)^2 \quad (2.7)$$

$$= \hat{\mathcal{H}}_0 + \mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B} + \frac{e^2}{8m_e} \sum_i (\mathbf{B} \times \mathbf{r}_i)^2 \quad (2.8)$$

The dominant perturbation to the original Hamiltonian $\hat{\mathcal{H}}_0$ is usually the term $\mu_B (\mathbf{L} + g\mathbf{S}) \cdot \mathbf{B}$ but, as we shall see, it sometimes vanishes. This is the effect of the atom's own magnetic moment and is known as the paramagnetic term. The third term, $(e^2/8m_e) \sum_i (\mathbf{B} \times \mathbf{r}_i)^2$, is due to the diamagnetic moment. These contributions will be discussed in greater detail in Section 2.3 (diamagnetism) and Section 2.4 (paramagnetism). In the following section we outline the effects which will need explaining.

2.2 Magnetic susceptibility

As shown in Section 1.1.4, for a linear material $\mathbf{M} = \chi \mathbf{H}$ where \mathbf{M} is the magnetic moment per volume (the magnetization) and χ is the magnetic susceptibility (dimensionless). Note that the definition of \mathbf{M} means that χ represents the magnetic moment induced by a magnetic field \mathbf{H} per unit volume. Magnetic susceptibilities are often tabulated in terms of the molar magnetic susceptibility, χ_m , where

$$\chi_m = \chi V_m. \quad (2.9)$$

In this equation V_m is the molar volume, the volume occupied by 1 mole (6.022×10^{23} formula units) of the substance. The molar volume (in m^3) is the relative atomic mass² of the substance (in kg) divided by the density ρ (in kg m^{-3}). The mass susceptibility χ_g is defined by

$$\chi_g = \frac{\chi}{\rho}, \quad (2.10)$$

and has units of $\text{m}^3 \text{kg}^{-1}$. The values of magnetic susceptibility for various substances are listed in Table 2.1. If the susceptibility is negative then the material is dominated by diamagnetism, if it is positive then the material is dominated by paramagnetism.

The magnetic susceptibilities of the first 60 elements in the periodic table are plotted in Fig. 2.1. Some of these are negative, indicative of the dominant rôle of diamagnetism as discussed in Section 2.3. However, some of the values are positive, indicative of paramagnetism and this effect will be discussed in Section 2.4.

¹Equation 2.4 relates \mathbf{B} and \mathbf{A} . However, for a given magnetic field \mathbf{B} , the magnetic vector potential \mathbf{A} is not uniquely determined; one can add to \mathbf{A} the gradient of a scalar potential and still end up with the same \mathbf{B} . The choice of \mathbf{A} that we make is known as a choice of gauge.

²The relative atomic mass is the mass of 1 mole. Note that relative atomic masses are usually tabulated in grams.

Table 2.1 The magnetic susceptibility χ and the molar magnetic susceptibility χ_m for various substances at 298 K. Water, benzene and NaCl are weakly diamagnetic (the susceptibility is negative). $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, Al and Na are paramagnetic (the susceptibility is positive).

	$\chi/10^{-6}$	$\chi_m/10^{-10}$ ($\text{m}^3 \text{mol}^{-1}$)
water	-90	-16.0
benzene	-7.2	-6.4
NaCl	-13.9	-3.75
graphite ()	-260	-31
graphite (\perp)	-3.8	-4.6
Cu	-1.1	-0.078
Ag	-2.4	-0.25
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	176	192
$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	2640	2.79×10^3
Al	22	2.2
Na	7.3	1.7

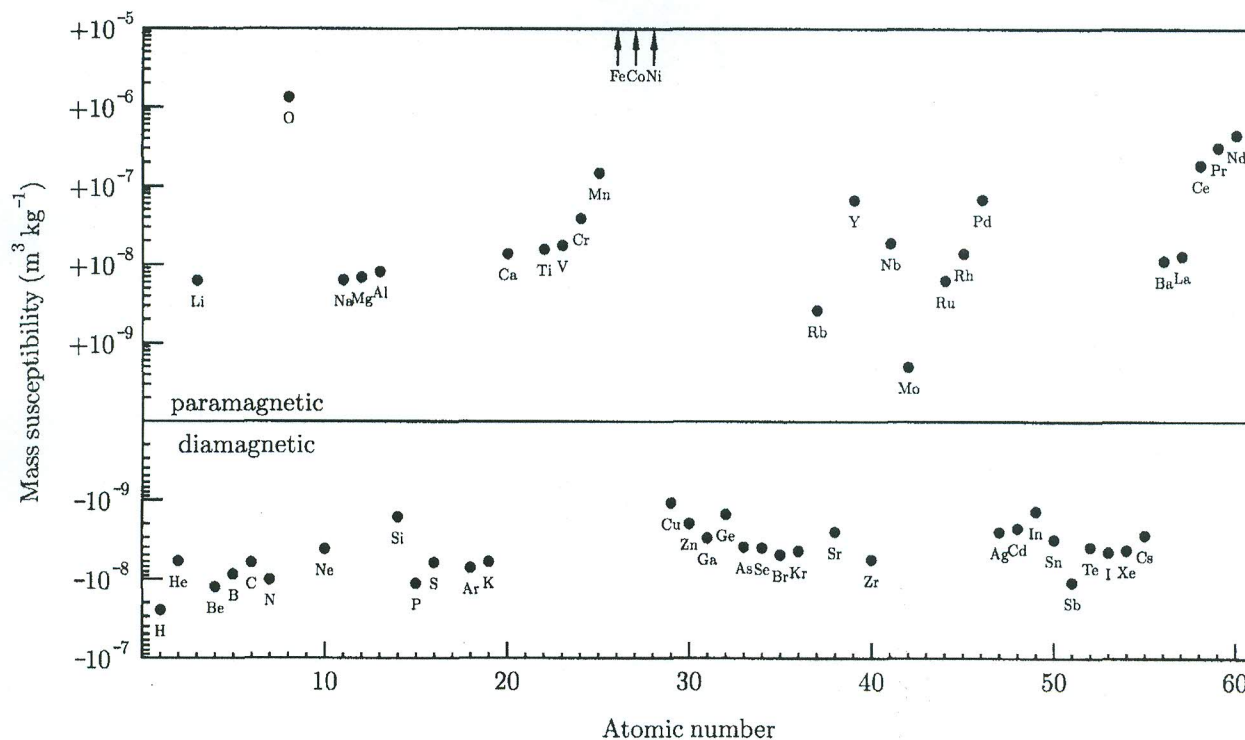


Fig. 2.1 The mass susceptibility of the first 60 elements in the periodic table at room temperature, plotted as a function of the atomic number. Fe, Co and Ni are ferromagnetic so that they have a spontaneous magnetization with no applied magnetic field.

2.3 Diamagnetism

³The prefix *dia* means 'against' or 'across' (and leads to words like *diagonal* and *diameter*).

⁴electromotive force

⁵ See the further reading.

All materials show some degree of diamagnetism,³ a weak, negative magnetic susceptibility. For a diamagnetic substance, a magnetic field induces a magnetic moment which opposes the applied magnetic field that caused it.

This effect is often discussed from a classical viewpoint: the action of a magnetic field on the orbital motion of an electron causes a back e.m.f.,⁴ which by Lenz's law opposes the magnetic field which causes it. However, the Bohr-van Leeuwen theorem described in the previous chapter should make us wary of such approaches which attempt to show that the application of a magnetic field to a classical system can induce a magnetic moment.⁵ The phenomenon of diamagnetism is entirely quantum mechanical and should be treated as such.

We can easily illustrate the effect using the quantum mechanical approach. Consider the case of an atom with no unfilled electronic shells, so that the paramagnetic term in eqn 2.8 can be ignored. If \mathbf{B} is parallel to the z axis, then $\mathbf{B} \times \mathbf{r}_i = B(-y_i, x_i, 0)$ and

$$(\mathbf{B} \times \mathbf{r}_i)^2 = B^2(x_i^2 + y_i^2) \quad (2.11)$$

so that the first-order shift in the ground state energy due to the diamagnetic term is

$$\Delta E_0 = \frac{e^2 B^2}{8m_e} \sum_{i=1}^Z \langle 0 | (x_i^2 + y_i^2) | 0 \rangle, \quad (2.12)$$

where $|0\rangle$ is the ground state wave function. If we assume a spherically symmetric atom,⁶ $\langle x_i^2 \rangle = \langle y_i^2 \rangle = \frac{1}{3} \langle r_i^2 \rangle$ then we have

$$\Delta E_0 = \frac{e^2 B^2}{12m_e} \sum_{i=1}^Z \langle 0 | r_i^2 | 0 \rangle. \quad (2.13)$$

Consider a solid composed of N ions (each with Z electrons of mass m) in volume V with all shells filled. To derive the magnetization (at $T = 0$), one can follow Appendix E, obtaining

$$M = -\frac{\partial F}{\partial B} = -\frac{N}{V} \frac{\partial \Delta E_0}{\partial B} = -\frac{N e^2 B}{6m_e} \sum_{i=1}^Z \langle r_i^2 \rangle, \quad (2.14)$$

where F is the Helmholtz function. Hence we can extract the diamagnetic susceptibility $\chi = M/H \approx \mu_0 M/B$ (assuming that $\chi \ll 1$). Following this procedure, we have the result that

$$\chi = -\frac{N e^2 \mu_0}{V 6m_e} \sum_{i=1}^Z \langle r_i^2 \rangle. \quad (2.15)$$

This expression has assumed first-order perturbation theory. (The second-order term will be considered in Section 2.4.4.) As the temperature is increased above zero, states above the ground state become progressively more important in determining the diamagnetic susceptibility, but this is a marginal effect. Diamagnetic susceptibilities are usually largely temperature independent.

This relation can be rather crudely tested by plotting the experimentally determined diamagnetic molar susceptibilities for various ions against $Z_{\text{eff}} r^2$, where Z_{eff} is the number of electrons in the outer shell of an ion⁷ and r is the measured ionic radius. The assumption is that all the electrons in the outer shell of the ion have roughly the same value of $\langle r_i \rangle^2$ so that

$$\sum_{i=1}^{Z_{\text{eff}}} \langle r_i^2 \rangle \approx Z_{\text{eff}} r^2. \quad (2.16)$$

The diamagnetic susceptibility of a number of ions is shown in Fig. 2.2. The experimental values are deduced by comparing the measured diamagnetic susceptibility of a range of ionic salts: NaF, NaCl, NaBr, KCl, KBr, ... The approach is inaccurate since not all the electrons in an ion have the same mean radius squared (so that eqn 2.16 is by no means exact), but the agreement is nevertheless quite impressive. Ions are chosen because, for example, Na and Cl atoms have unpaired electrons but Na^+ and Cl^- ions are both closed shell structures, similar to those of Ne and Ar (see the periodic table in Fig. 2.13 below for reference). Thus paramagnetic effects, which would dominate the magnetic response of the atoms, can be ignored in the ions.

Relatively large and anisotropic diamagnetic susceptibilities are observed in molecules with delocalized π electrons, such as naphthalene and graphite. Naphthalene consists of two benzene molecules joined along one side (Fig. 2.3(a)). The π electrons are very mobile and induced currents can run round the edge of the ring, producing a large diamagnetic susceptibility which is largest if the magnetic field is applied perpendicular to the plane of the ring.

⁶This is a good assumption if the total angular momentum J is zero.

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⁷For an ion, this value is different from the atomic number Z , so we use the symbol Z_{eff} for an 'effective' atomic number. We are ignoring electrons in inner shells.

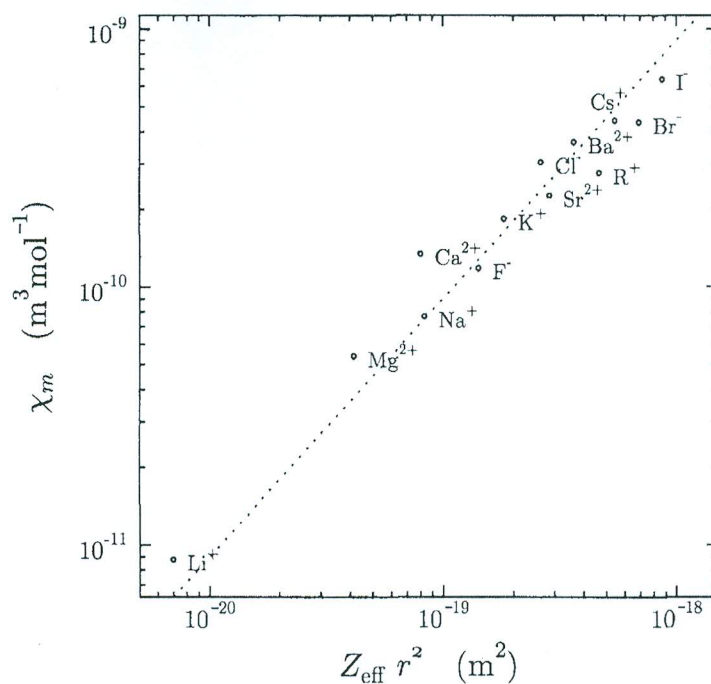


Fig. 2.2 The measured diamagnetic molar susceptibilities χ_m of various ions plotted against $Z_{\text{eff}} r^2$, where Z_{eff} is the number of electrons in the ion and r is a measured ionic radius.

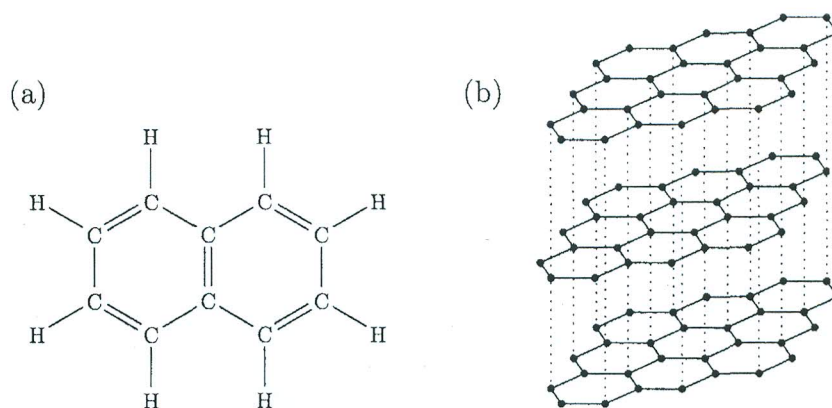


Fig. 2.3 (a) Naphthalene consists of two fused benzene rings. (b) Graphite consists of sheets of hexagonal layers. The carbon atoms are shown as black blobs. The carbon atoms are in registry in alternate, not adjacent planes (as shown by the vertical dotted lines).

The effective ring diameter is several times larger than an atomic diameter and so the effect is large. This is also true for graphite which consists of loosely bound sheets of hexagonal layers (Fig. 2.3(b)). The diamagnetic susceptibility is much larger if the magnetic field is applied perpendicular to the layers than if it is applied in the parallel direction.

Diamagnetism is present in all materials, but it is a weak effect which can either be ignored or is a small correction to a larger effect.

2.4 Paramagnetism

Paramagnetism⁸ corresponds to a positive susceptibility so that an applied magnetic field induces a magnetization which aligns parallel *with* the applied magnetic field which caused it. In the previous section we considered materials which contained no unpaired electrons, and thus the atoms or molecules had no magnetic moment unless a field was applied. Here we will be concerned with atoms that *do* have a non-zero magnetic moment because of unpaired electrons. Without an applied magnetic field, these magnetic moments point in random directions because the magnetic moments on neighbouring atoms interact only very weakly with each other and can be assumed to be independent. The application of a magnetic field lines them up, the degree of lining up (and hence the induced magnetization) depending on the strength of the applied magnetic field.

The magnetic moment on an atom is associated with its **total angular momentum** \mathbf{J} which is a sum of the orbital angular momentum \mathbf{L} and the spin angular momentum \mathbf{S} , so that

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (2.17)$$

Here, as throughout this book, these quantities are measured in units of \hbar . The way in which the spin and orbital parts of the angular momentum combine will be considered in detail in the following sections. In this section we will just assume that each atom has a magnetic moment of magnitude μ .

Although an increase of magnetic field will tend to line up the spins, an increase of temperature will randomize them. We therefore expect that the magnetization of a paramagnetic material will depend on the ratio B/T . The paramagnetic effect is in general much stronger than the diamagnetic effect, although the diamagnetism is always present as a weak negative contribution.

2.4.1 Semiclassical treatment of paramagnetism

We begin with a semiclassical treatment of paramagnetism (which as we will see below corresponds to $J = \infty$) in which we ignore the fact that magnetic moments can point only along certain directions because of quantization. Consider magnetic moments lying at an angle between θ and $\theta + d\theta$ to the applied field \mathbf{B} which is assumed without loss of generality to be along the z direction. These have an energy $-\mu B \cos \theta$ and have a net magnetic moment along \mathbf{B} equal to $\mu \cos \theta$. If the magnetic moments could choose any direction to point along at random, the fraction which would have an angle between θ and $\theta + d\theta$ would be proportional to the area of the annulus shown in Fig. 2.4 which is $2\pi \sin \theta d\theta$ if the sphere has unit radius. The total surface area of the unit sphere is 4π so the fraction is $\frac{1}{2} \sin \theta d\theta$. The probability of having angle between θ and $\theta + d\theta$ at temperature T is then simply proportional to the product of this statistical factor, $\frac{1}{2} \sin \theta d\theta$, and the Boltzmann factor $\exp(\mu B \cos \theta / k_B T)$ where k_B is Boltzmann's constant. The average moment

⁸The prefix *para* means 'with' or 'along' and leads to English words such as *parallel*.

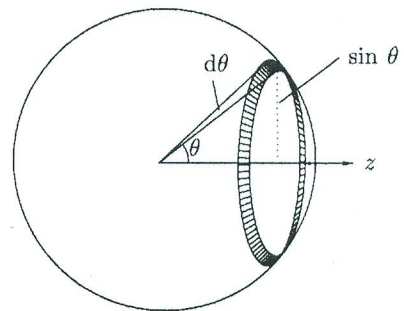


Fig. 2.4 To calculate the average magnetic moment of a paramagnetic material, consider the probability that the moment lies between angles θ and $\theta + d\theta$ to the z axis. This is proportional to the area of the annulus on the unit sphere, shown shaded, which is $2\pi \sin \theta d\theta$.