

## FoP3B Part I Lecture 5: Diamagnetism

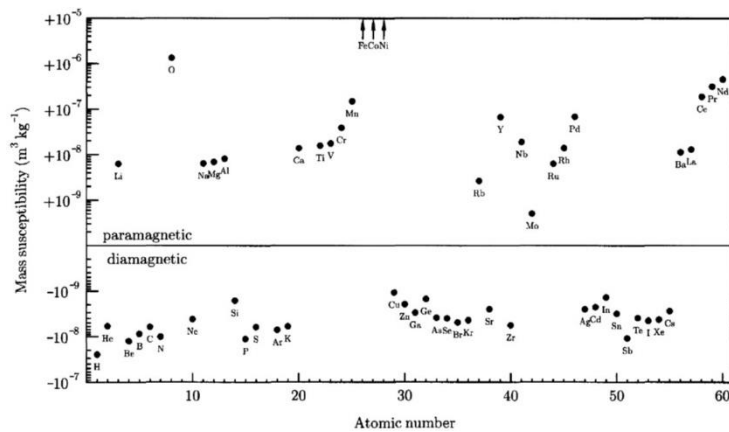


Figure 1

Figure 1 shows the mass susceptibility (i.e. magnetic susceptibility divided by the material density) for various elements in the periodic table. The majority of elements are either weakly magnetic (i.e. paramagnetic with  $\chi > 0$ ) or diamagnetic ( $\chi < 0$ )<sup>1</sup>. In this lecture we will explore diamagnetism, using both classical and quantum physics.

### Langevin's theory of diamagnetism

The classical theory of diamagnetism is due to Paul Langevin. Consider the precession of a magnetic moment  $\mu$  in a  $\mathbf{B}$ -field applied along the  $z$ -axis (Figure 2).

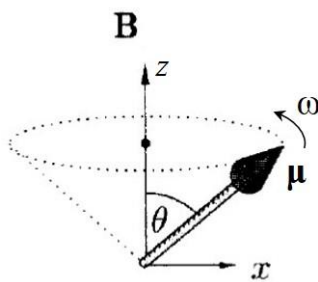


Figure 2

From the precession formula  $\frac{d\mu}{dt} = -\gamma(\mu \times \mathbf{B})$ :

$$\frac{d\mu_x}{dt} = -\gamma B \mu_y ; \quad \frac{d\mu_y}{dt} = \gamma B \mu_x \quad \text{and} \quad \frac{d\mu_z}{dt} = 0$$

The fact that the  $z$ -component of  $\mu$  is unchanged with time is indicative of precessional motion. If at time  $t = 0$  the moment  $\mu$  is in the  $xz$ -plane, the above differential equations give:

$$\mu_x(t) = \mu \sin \theta \cos(\omega t) ; \quad \mu_y(t) = \mu \sin \theta \sin(\omega t)$$

Here the angular frequency  $\omega = \gamma B = \frac{eB}{2m}$  is known as the **Larmor precession frequency**. We saw in the previous lecture that electrons in a circular orbit generate magnetic moments. In the presence of a magnetic field, in addition to the circular motion, there will also be Larmor precessional motion which generates its own magnetic moment. From Figure 2 it is clear that the precessional moment is anti-parallel to the  $\mathbf{B}$ -field (recall that we define current as the flow of *positive* charge, while electrons are negatively charged). Therefore, there is a magnetic field generated by precession that *opposes* the external field. This is the origin of diamagnetism according to classical physics. In some cases, this is described as being similar to **Lenz's law** from the theory of electromagnetic induction, although this is misleading, since Lenz's law only applies to time-dependent magnetic fields, whereas in our case the  $\mathbf{B}$ -field can be static.

Let us calculate the magnitude of the precessional magnetic moment. The precession period is  $T = 2\pi/\omega = 4\pi m/eB$  and the precession current is  $I = e/T = e^2 B/4\pi m$ . To calculate the induced moment we need to multiply  $-I$  by the area of current loop, i.e.  $\pi \langle \rho^2 \rangle$ , where  $\langle \rho^2 \rangle$  is the mean square radius of the precessing electron from the atom nucleus. Note the minus sign in  $-I$  is to

<sup>1</sup> In fact, it is a misconception that magnetism is a rare phenomenon!

indicate that the induced moment opposes the applied  $\mathbf{B}$ -field. For a spherically symmetric atom  $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$  (i.e. we cannot distinguish between  $x, y$  and  $z$ -directions). Since  $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$ , we have  $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle = 2/3 \langle r^2 \rangle$ . The magnetic moment of a single electron is  $-I(\pi \langle \rho^2 \rangle)$  or  $-e^2 B \langle r^2 \rangle / 6m$ . Assume there are  $n$  atoms/ions per unit volume each with  $Z$  electrons. The magnetisation  $M$  is therefore:

$$M = -\frac{ne^2 Z B \langle r^2 \rangle}{6m}$$

For weak magnetisation  $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \approx \mu_0 \mathbf{H}$ . Therefore  $\chi = M/H = \mu_0 M/B$ . The diamagnetic susceptibility is then:

$$\chi = -\frac{ne^2 \mu_0 Z \langle r^2 \rangle}{6m}$$

Note that the diamagnetic susceptibility is independent of temperature.

Although it may appear that diamagnetism is compatible with classical physics, we still have to keep in mind the Bohr-van Leeuwen theorem, which states that the equilibrium magnetisation is zero for a classical system. Figure 3 shows how we might reconcile these two seemingly conflicting results; the Larmor precession orbits of all the internal electrons within the solid reinforce one another, such that their net effect can be represented by a larger orbit taken in the same sense (i.e. anti-clockwise) along the surface boundary of the solid.

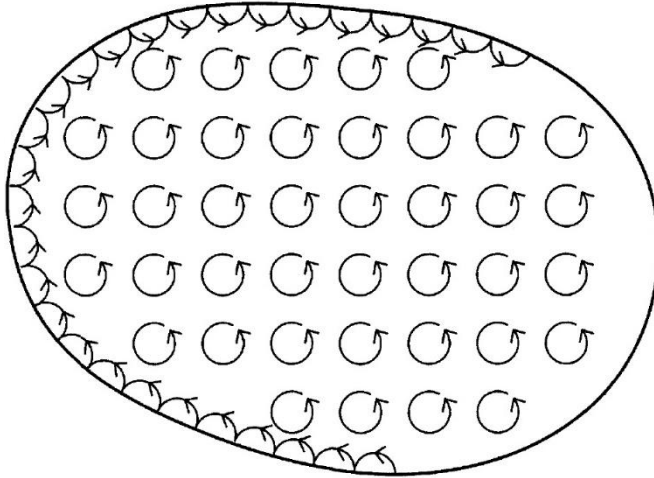


Figure 3

However, those electrons that are close to the surface can complete only half of the Larmor precession orbit (known as *skipping orbits*), and *overall* these run in the opposite sense (i.e. clockwise) to the internal electron orbits. The induced magnetic moment from the internal electrons are therefore cancelled by the surface electrons, giving a zero net magnetisation as required. We must therefore look to quantum mechanics to find the exact origin of diamagnetism.

### Quantum Mechanical Treatment

We start by considering the Hamiltonian for a single electron in a magnetic field  $\mathbf{B}$ :

$$\hat{H} = \frac{(\mathbf{p} + e\mathbf{A})^2}{2m} + V + g_s \gamma \mathbf{B} \cdot \mathbf{s}$$

The first term is the kinetic energy with the momentum  $\mathbf{p}$  replaced by the canonical momentum  $(\mathbf{p} + e\mathbf{A})$ , where  $\mathbf{B} = \nabla \times \mathbf{A}$  and  $\mathbf{A}$  is the magnetic vector potential. The canonical momentum is due to the Lorentz force acting on the electron; its derivation can be found in the Supplementary Reading on DUO. The second term in the Hamiltonian is the standard potential energy  $V$ . The final term is the energy due to the electron spin angular momentum  $\mathbf{s}$ ; this has the form of

energy of a magnetic moment  $\boldsymbol{\mu}$  in an applied field, i.e.  $-\boldsymbol{\mu} \cdot \mathbf{B} = \gamma \mathbf{B} \cdot \mathbf{l}$ , with  $\mathbf{s}$  replacing the angular momentum  $\mathbf{l}$ . The term  $g_s$  is the Landé g-factor and has a value that is very nearly 2.

If we set the gauge as  $\mathbf{A}(\mathbf{r}) = (\mathbf{B} \times \mathbf{r})/2$ , then:

$$\hat{H} = \left( \frac{\mathbf{p}^2}{2m} + V \right) + \frac{e}{m} (\mathbf{p} \cdot \mathbf{A}) + g_s \gamma \mathbf{B} \cdot \mathbf{s} + \frac{e^2 \mathbf{A}^2}{2m}$$

But  $\frac{e}{m} (\mathbf{p} \cdot \mathbf{A}) = \frac{e}{2m} \mathbf{p} \cdot (\mathbf{B} \times \mathbf{r}) = \gamma \mathbf{B} \cdot (\mathbf{r} \times \mathbf{p})$  and  $\mathbf{l} = \mathbf{r} \times \mathbf{p}$ , so that:

$$\hat{H} = \left( \frac{\mathbf{p}^2}{2m} + V \right) + \gamma \mathbf{B} \cdot (\mathbf{l} + g_s \mathbf{s}) + \frac{e^2}{8m} (\mathbf{B} \times \mathbf{r})^2$$

The second and third terms represent the magnetic contribution to the standard Hamiltonian. They are known as the paramagnetic and diamagnetic terms respectively. Let us examine the latter in more detail. By first order perturbation theory the energy change ( $\Delta E$ ) to the ground state wavefunction  $|0\rangle$  due to the diamagnetic term is (see Lecture 2):

$$\Delta E = \frac{e^2}{8m} \langle 0 | (\mathbf{B} \times \mathbf{r})^2 | 0 \rangle$$

If  $\mathbf{B}$  is along the  $z$ -axis then  $(\mathbf{B} \times \mathbf{r})^2 = B^2(x^2 + y^2)$ . Therefore:

$$\Delta E = \frac{e^2 B^2}{8m} \{ \langle 0 | x^2 | 0 \rangle + \langle 0 | y^2 | 0 \rangle \}$$

The first and second terms within the curly brackets are the expectation values for  $x^2$  and  $y^2$  respectively, i.e.  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ . Since  $\langle x^2 \rangle = \langle y^2 \rangle = \langle r^2 \rangle / 3$  for electrons in spherical atoms:

$$\Delta E = \frac{e^2 B^2}{12m} \langle r^2 \rangle$$

Note that the energy change  $\Delta E$  is always positive. Hence the diamagnetic term will always repel the applied  $\mathbf{B}$ -field in order to lower the energy of the solid. The magnetic moment  $\mu = -d(\Delta E)/dB$ , so that for  $n$  atoms/ions per unit volume each with  $Z$  electrons the magnetisation is  $M = -\frac{ne^2 Z B}{6m} \langle r^2 \rangle$ . For weak magnetisation (i.e.  $\chi = \mu_0 M/B$ ):

$$\chi = -\frac{ne^2 \mu_0 Z \langle r^2 \rangle}{6m}$$

Fortuitously, this is the same result as derived from Langevin theory! However, the origins are rather different. Diamagnetism is due to a  $\frac{e^2}{8m} (\mathbf{B} \times \mathbf{r})^2$  term in the Hamiltonian, which is present in every solid. In some solids the paramagnetic term  $\gamma \mathbf{B} \cdot (\mathbf{l} + g_s \mathbf{s})$  may be larger, thereby giving rise to net paramagnetic behaviour, although the weaker diamagnetic contribution will still be present.

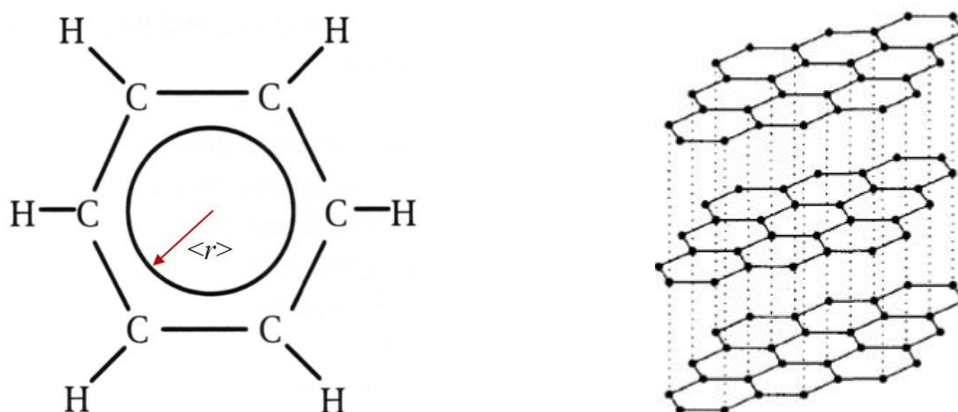
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<sup>2</sup> We use the cyclic permutation property of the scalar product between three vectors  $\mathbf{a}, \mathbf{b}$  and  $\mathbf{c}$ , i.e.  $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{b} \cdot (\mathbf{c} \times \mathbf{a}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})$ .

### *Delocalised electrons and magnetic anisotropy*

An interesting situation arises for materials, such as a benzene molecule or graphite, that contain so-called *delocalised electrons*. Taking benzene ( $\text{C}_6\text{H}_6$ ) as an example we have a hexagonal arrangement of carbon atoms with each carbon atom bonded to a hydrogen atom (Figure 4). For a stable electronic configuration carbon has to form four covalent bonds. This can be achieved by carbon forming a double bond with either one of its neighbouring carbon atoms. There are therefore two possible structural configurations; however, quantum mechanics predicts that the electron will be delocalised, rather than being confined to a single double bond. The delocalised electron, also known as  $\pi$ -electrons, spreads over the entire molecule (Figure 4), so that its radius  $\langle r \rangle$  is now the size of the molecule, rather than a single atom. Since the susceptibility depends on  $\langle r^2 \rangle$  compounds such as benzene and graphite show strong diamagnetic behaviour.

There is also a subtlety arising from the fact that the diamagnetism is ultimately due to the  $\frac{e^2}{8m}(\mathbf{B} \times \mathbf{r})^2$  Hamiltonian term. If the  $\mathbf{B}$ -field is applied parallel to the benzene molecule or graphite planes then  $\mathbf{B} \times \mathbf{r} = \mathbf{0}$ , so that the susceptibility  $\chi$  along this direction is zero. The absolute value of  $\chi$  will however be a maximum for  $\mathbf{B}$ -fields that are normal to the benzene molecule or graphite planes. This phenomenon, where the magnetic response depends on the direction of the applied  $\mathbf{B}$ -field is known as **magnetic anisotropy**.



**Figure 4:** A benzene molecule (left) and graphite solid (right)