

3.1 Magnetism at the atomic level

We learned in Chapter 1 that magnetic fields are generated by electric currents. Given that there are no wires leading into or out of permanent magnets, you may well ask, “Where are the currents?” At the atomic level, the electric currents come from the motions of the electrons. From here quantum mechanics quickly gets esoteric, but some rudimentary understanding is helpful. In this chapter we will cover the bare minimum necessary to grasp the essentials of rock magnetism.

In Chapter 1 we took the classical (pre-quantum mechanics) approach and suggested that the orbit of an electron about the nucleus could be considered a tiny electric current with a correspondingly tiny magnetic moment. But quantum physics tells us that this “planetary” view of the atom cannot be true. An electron zipping around a nucleus would generate radio waves, losing energy and eventually would crash into the nucleus.

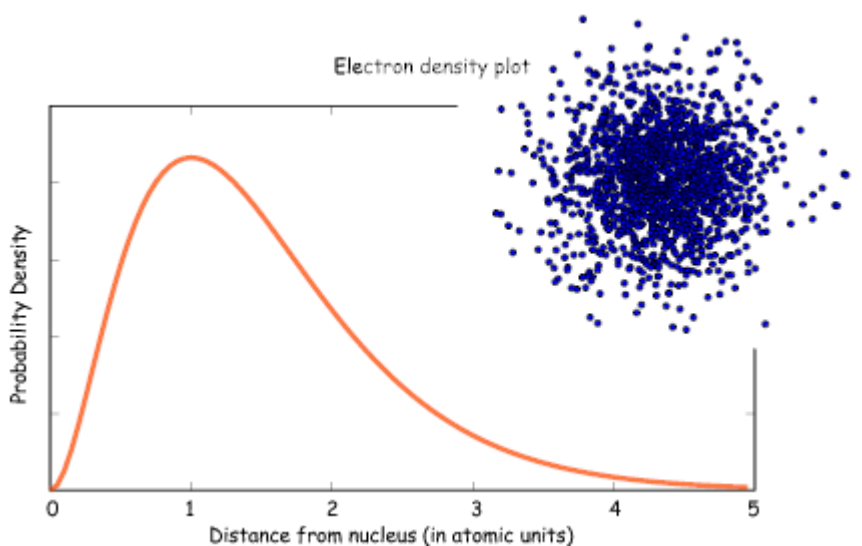


Figure 3.1: Plot of radial distribution and “dot-density” for the 1s electron shell.

Apparently, this does not happen, so the classical approach is fatally flawed and we must turn to quantum mechanics.

In quantum mechanics, electronic motion is stabilized by the fact that electrons can only have certain energy states; they are quantized. The energy of a given electron can be described in terms of solutions, Ψ , to something called Schrödinger’s wave equation. The function $\Psi(r,\theta,\phi)$ gives the probability of finding an electron at a given position. [Remember from Chapter 2 that r,θ,ϕ are the three spherical coordinates.] It depends on three special quantum numbers (n,l,m):

$$\Psi_{r,\theta,\phi} = R_n^l(r)Y_l^m(\phi, \theta), (3.1)$$

The number n is the so-called “principal” quantum number. The $R_n^l(r)$ are functions specific to the element in question and the energy state of the electron n . It is evaluated at an effective radius r in atomic units. The Y_l^m are a fully normalized complex representation of the spherical harmonics introduced in Section 2.2. For each level n , the number l ranges from 0 to $n-1$ and m from l backwards to $-l$.

The lowest energy of the quantum wave equations is found by setting n equal to unity and both l and m to zero. Under these conditions, the solution to the wave equation is given by:

$$R_{1,0} = 2Z^{\frac{3}{2}}e^{-\rho/2},$$

$$Y_{0,0} = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}} (3.2)$$

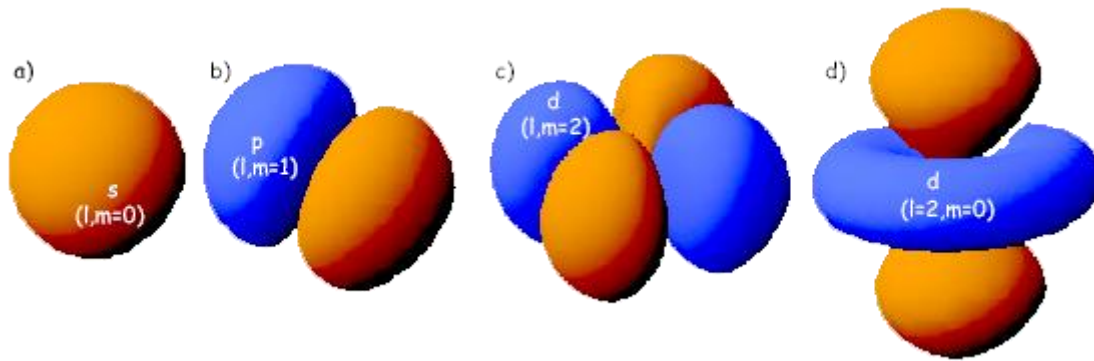
where Z is the atomic number and ρ is $2Zr/n$. Note that at this energy level, there is no dependence of Y on ϕ or θ . Substituting these two equations into Equation 3.1 gives the probability density Ψ for an electron as a function of radius of r . This is sketched as the line in Figure 3.1. Another representation of the same idea is shown in the inset, whereby the density of dots at a given radius reflects the probability distribution shown by the solid curve. The highest dot density is found at a radius of about one atomic unit, tapering off the farther away from the center of the atom. Because there is no dependence on θ or ϕ the probability distribution is a spherical shell. All the $l,m = 0$ shells are spherical and are often referred to as the 1s, 2s, 3s shells, where the numbers are the energy levels n . A surface with equal probability is a sphere and example of one such shell is shown in Figure 3.2a.

For $l = 1$, m will have values of $-1, 0$ and 1 and the $Y_l^m(\phi,\theta)$ s are given by:

$$Y_1^{-1} = \frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\phi}, \quad Y_1^0 = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta, \quad Y_1^1 = \frac{-1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}.$$

Shells with $l = 1$ depend not only on radial distance but also on the angles ϕ and θ , so they are not spheres, but more complicated shapes. A surface of equal probability for one such shell (the $m = 1$ shell) is shown in Figure 3.2b. Shells with $l = 1$ are called the “p” shells.

As might be expected, the shells for $l = 2$ are even more complicated than for $l = 1$. These shells are called “d” shells and two examples are shown in Figure 3.2c and d.



Examples of surfaces of equal probability of the first three shells ($l = 1, 2, 3$).
 Figure 3.2: Surfaces created with Orbital Viewer.

Returning to the tiny circuit idea, somehow the motion of the electrons in their shells acts like an electronic circuit and creates a magnetic moment. In quantum mechanics, the angular momentum vector of the electron L is quantized, for example as integer multiples of \hbar , the “reduced” Planck’s constant (or $h / 2\pi$ where $h = 6.63 \times 10^{-34}$ Js). The magnetic moment arising from the orbital angular momentum is given by:

$$|\mathbf{m}| = -\frac{q_e}{2\mu_e} |\mathbf{L}|,$$

where μ_e is the mass of an electron (9.11×10^{-31} kg), $q_e = -1.69 \times 10^{-19}$ C. The smallest value of L is \hbar so the fundamental unit of magnetic moment arising from the orbit of electrons is given by:

$$|\mathbf{m}_b| = \frac{\hbar q_e}{2\mu_e} = 9.27 \times 10^{-24} \frac{\text{kg m}^2}{\text{s}} \cdot \frac{\text{C}}{\text{kg}} = 9.27 \times 10^{-24} \text{Am}^2. \quad (3.3)$$

This is known as the Bohr magneton.

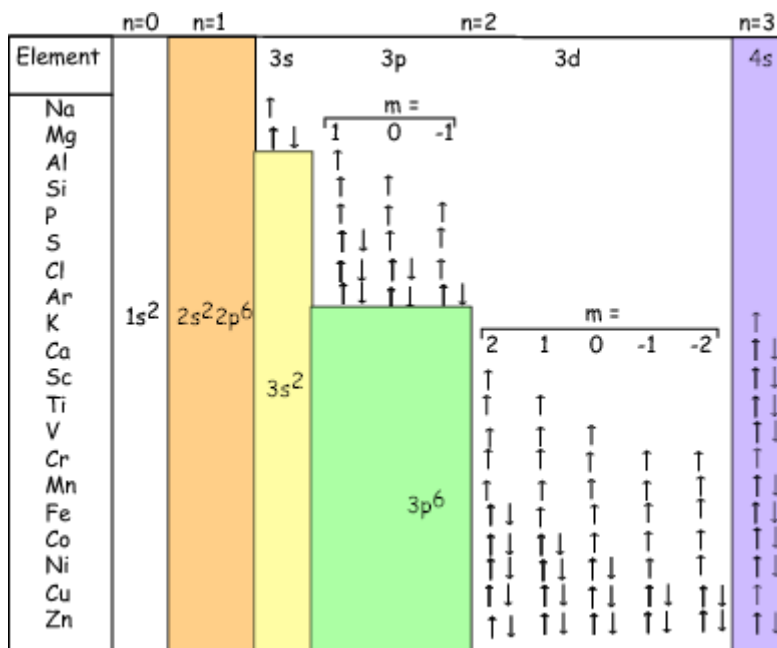


Figure 3.3: Electronic structure of elements from Na to Zn.

So far we have not mentioned one last quantum number, s . This is the “spin” of the electron and has a value of $\pm 1/2$. The spin itself produces a magnetic moment which is given by $2sm_b$, hence is numerically identical to that produced by the orbit.

Atoms have the same number of electrons as protons in order to preserve charge balance. Hydrogen has but one lonely electron which in its lowest energy state sits in the $1s$ electronic shell. Helium has a happy pair, so where does the second electron go? To fill in their electronic shells, atoms follow three rules:

1. No two electrons may have the same set of quantum numbers. This is Pauli’s exclusion principle. Because spin (s) can be $\pm 1/2$, two electrons fit in one orbital. When a single electron occupies a given orbital, it is called “unpaired” and has a magnetic moment of $1 m_b$.
2. Orbitals are filled in order of increasing energy. The energy state of a given orbital is dependent on the context (whether the atom is bound to other atoms or not), but in general they will be filled according to the scheme shown in Figure 3.3.
3. Electrons are added so that the spins remain as parallel as possible (Hund’s rule). Notice in Figure 3.3 that when filling the third energy level ($n = 3$), all five d shells are filled with one kind of spin (say, all up, or $+1/2$), before the electrons begin to pair up. Also, because the energies of the shells change somewhat according to the context they are in, the $4s$ shell will actually give up an electron to a d shell, before the d shells begin to pair up. Hund’s rule gives the atoms with some d shell electrons (the so-called “transition

elements”, e.g., Cr, Mn, Fe, Co and Ni) the possibility of large magnetic moments.

Each unpaired spin has a moment of one Bohr magneton m_b . The elements with the most unpaired spins are the transition elements which are responsible for most of the paramagnetic behavior observed in rocks. For example, in Figure 3.3 we see that Mn has a structure of: $(1s^2 2s^2 2p^6 3s^2 3p^6) 3d^5 4s^2$, hence has five unpaired spins and a net moment of 5 m_b . Fe has a structure of $(1s^2 2s^2 2p^6 3s^2 3p^6) 3d^6 4s^2$ with a net moment of 4 m_b . In minerals, the transition elements are in a variety of oxidation states. Fe commonly occurs as Fe^{2+} and Fe^{3+} . When losing electrons to form ions, transition metals lose the 4s electrons first, so we have for example, Fe^{3+} with a structure of $(1s^2 2s^2 2p^6 3s^2 3p^6) 3d^5$, or 5 m_b . Similarly Fe^{2+} has 4 m_b and Ti^{4+} has no unpaired spins. Iron is the main magnetic species in geological materials, but Mn^{2+} (5 m_b) and Cr^{3+} (3 m_b) occur in trace amounts.