Magnetism of isolated electrons and atoms.

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The magnetic moments in solids are essentially associated with the angular momentum of electrons, which has two distinct sources – orbital motion and spin. The reality of the connection between magnetism and angular momentum is demonstrated by the Einstein – de Haas experiment. The microscopic theory of magnetism is based on the quantum mechanics of electronic angular momentum, and the proportionality between angular momentum and magnetic moment is a factor two greater for spin than orbit, so that a unit $\frac{1}{2}\hbar$ [Js] of spin angular momentum or $\hbar$ of orbital angular momentum both give rise to a magnetic moment of one Bohr magneton μ_B, $(e\hbar/2m_e)$ or $9.27 \ 10^{-24}$ Am^2. In quantum mechanics the spin angular momentum of the electron, with quantum number $s = \frac{1}{2}$ is conveniently represented by the $2 \nabla 2$ Pauli spin matrices, and the orbital angular momentum with quantum number $l = 0, 1, 2 \ldots$ is represented by $(2l + 1) \times (2l + 1)$ matrices. The total magnetic moment **m** is therefore represented by the operator $(\mathbf{l} + 2\mathbf{s})\mu_B$. The two types of angular momentum are coupled by the spin–orbit interaction $\times \mathbf{l}.\mathbf{s}$.

The description of magnetism in solids is fundamentally different, depending on whether the electrons are regarded as localized on ion cores where they obey Boltzmann statistics, or delocalized in energy bands where they obey Fermi-Dirac statistics. Free electrons follow cyclotron orbits in a magnetic field, whereas bound electrons undergo Larmor precession, which gives rise to orbital diamagnetism.

A starting point for discussion of magnetism in metals is the free-electron model that leads to temperature-independent Pauli paramagnetism and Landau diamagnetism. By contrast, localized noninteracting $s = \frac{1}{2}$ electrons exhibit Curie paramagnetism, varying as $1/T$.

The localized picture is based on the magnetism of isolated multi-electron atoms or ions. Atomic physics is concerned with the energy levels of an isolated atom or ion. The starting point is the quantum mechanics of a single electron in a central potential, which leads to classification of the one-electron states in terms of four quantum numbers l, s, m_l and m_s. The first three; l, s and m_l denote an orbital, which can be occupied by two electrons with opposite spin, $m_s = \pm \frac{1}{2}$. The individual electrons' spin and orbital angular momenta are coupled in an isolated many-electron ion to give total spin and orbital quantum numbers L and S, where only the electrons in partially-filled shells contribute. Spin-orbit coupling then operates to split the energy levels into a series of J-multiplets, the lowest of which is specified by Hund's rules. Normally it is only necessary to consider the Hund's-rule ground state to understand the magnetism. The Curie-law susceptibility, $\chi = C /T$, is calculated for a general value of J (Brillouin theory), and in the classical limit (Langevin theory).

When placed in a solid, the ion experiences a crystal field due to the charge environment, which disturbs the spin-orbit coupling, leaving either S or J as the appropriate quantum number. The crystal field creates new one-electron orbitals, which are linear combinations of the m_l states. It modifies the structure of the lowest M_S or M_J magnetic sublevels, which are split by the Zeeman interaction and it introduces single-ion anisotropy via spin-orbit interaction.

Background Reading;
J. M. D. Coey, *Magnetism and Magnetic Materials,* Cambridge University Press 2010, Chapters 3, 4.