2.1: Magnetic resonance of the free electron

The magnetic moment of the free electron

As an elementary particle, the electron has an intrinsic angular momentum called spin. The spin quantum number is $S = 1/2$, so that in an external magnetic field along z, only two possible values can be observed for the z component of this angular momentum, $+\hbar/2$, corresponding to magnetic quantum number $m_S = +1/2(\alpha$ state $)$ and $-\hbar/2$, corresponding to magnetic quantum number $m_S = -1/2$ (β state). The energy difference between the corresponding two states of the electron results from the magnetic moment associated with spin. For a classical rotating particle with elementary charge e, angular momentum $J = \hbar S$ and mass m_e, this magnetic moment computes to

$$\vec{\mu}_{\text{classical}} = \frac{e}{2m_e}\vec{J} \tag{2.1.1}$$

The charge-to-mass ratio e/m_e is much larger for the electron than the corresponding ratio for a nucleus, where it is of the order of $-e/m_p$, where m_p is the proton mass. By introducing the Bohr magneton $\mu_{\mathrm{B}} = \hbar e/\left(2m_e\right) = 9.27400915(23) \times 10^{-24}\ \mathrm{J\ T^{-1}}$ and the quantum-mechanical correction factor g, we can rewrite Eq. (2.1) as

$$\vec{\mu}_{\mathrm{e}} = g\mu_{\mathrm{B}}\vec{S} \tag{2.1.2}$$

Dirac-relativistic quantum mechanics provides $g = 2$, a correction that can also be found in a non-relativistic derivation. Exact measurements have shown that the g value of a free electron deviates slightly from $g = 2$. The necessary correction can be derived by quantum electrodynamics, leading to $g_e = 2.00231930437378(2.)$The energy difference between the two spin states of a free electron in an external magnetic field B_0 is given by

$$\hbar\omega_S = g_e\mu_{\mathrm{B}}B_0 \tag{2.1.3}$$

so that the gyromagnetic ratio of the free electron is $\gamma_e = -g_e\mu_{\mathrm{B}}/\hbar$. This gyromagnetic ratio corresponds to a resonance frequency of $28.025\mathrm{GHz}$at a field of $1\ \mathrm{T}$, which is by a factor of about 658 larger than the nuclear Zeeman frequency of a proton.

Differences between EPR and NMR spectroscopy

Most of the differences between NMR and EPR spectroscopy result from this much larger magnetic moment of the electron. Boltzmann polarization is larger by this factor and at the same magnetic field the detected photons have an energy larger by this factor. Relaxation times are roughly by a factor 658^2 shorter, allowing for much faster repetition of EPR experiments compared to NMR experiments. As a result, EPR spectroscopy is much more sensitive. Standard instrumentation with an electromagnet working at a field of about $0.35\ \mathrm{T}$ and at microwave frequencies of about $9.5\mathrm{GHz}$ (X band) can detect about 10^{10} spins, if the sample has negligible dielectric microwave losses. In aqueous solution, organic radicals can be detected at concentrations down to $10\mathrm{nM}$ in a measurement time of a few minutes.

Due to the large magnetic moment of the electron spin the high-temperature approximation may be violated without using exotic equipment. The spin transition energy of a free electron matches thermal energy $k_{\mathrm{B}}T$ at a temperature of $4.5\ \mathrm{K}$ and a field of about $3.35\ \mathrm{T}$ corresponding to a frequency of about $94\mathrm{GHz}$ (W band). Likewise, the high-field approximation may break down. The dipole-dipole interaction between two electron spins is by a factor of 658^2 larger than between two protons and two unpaired electrons can come closer to each other than two protons. The zero-field splitting that results from such coupling can amount to a significant fraction of the electron Zeeman interaction or can even exceed it at the magnetic fields, where EPR experiments are usually performed $(0.1 - 10\ \mathrm{T})$. The hyperfine coupling between an electron and a nucleus can easily exceed the nuclear Zeeman frequency, which leads to breakdown of the high-field approximation for the nuclear spin.