

Figure 13.14: Chemical and magnetic equivalence.

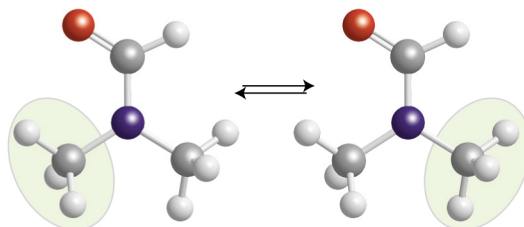


Figure 13.15: Conformational conversion: the protons of the two methyl groups are magnetically inequivalent but if the rotation about the C-N bond is fast enough, they become, effectively, equivalent.

13.3 Electron paramagnetic resonance spectroscopy

Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR), is the electronic equivalent of NMR. The magnetic moment of the electron is given by

$$\hat{\mathbf{m}} = -g_e \frac{\mu_B}{\hbar} \hat{\mathbf{s}} \quad (13.36)$$

where $\hat{\mathbf{s}}$ is the vector spin operator of the electron,

$$\mu_B = \frac{e\hbar}{2m_e} \quad (13.37)$$

is the Bohr magneton, and g_e is the electron g -value. The g -value of an isolated electron is $g_e = 2.0023$. While the value $g_e = 2$ is obtained from the rotational symmetry of a an isolated electron (it also appears naturally in relativistic quantum mechanics, but it is *not* a relativistic effect), the additional 0.0023 is a quantum electrodynamical effect. As for nuclei, the magnetic moment of an electron interacts with an external magnetic field as described in Sec. 13.1 above. However, since the Bohr magneton is almost 2000 times greater than the nuclear magneton,

$$\frac{\mu_B}{\mu_N} = \frac{e\hbar/2m_e}{e\hbar/2m_p} = \frac{m_p}{m_e} \approx 1836 \quad (13.38)$$

much stronger signals are obtained in EPR than in NMR. This implies that we may use significantly weaker fields in EPR. The typical EPR magnetic field strength is about 0.3 T (compared with 10 T in NMR), which gives resonance at about 9 GHz.

Exercise 13.10 What is the wavelength corresponding to the resonance frequency 9 GHz? ■

Despite the stronger signals in EPR, it has limited applicability compared with NMR, since EPR requires *unpaired electron spins*—i.e., it can only be applied to open-shell systems such as radicals and d-metal complexes. Still, EPR is an important tool in biology.

According to Sec. 13.1, the α ($m_s = +\frac{1}{2}$) and β ($m_s = -\frac{1}{2}$) spin states of the electron have different energies in a magnetic field along the z -direction

$$E_\alpha = \frac{1}{2}g_e\mu_B B_0 > E_\beta = -\frac{1}{2}g_e\mu_B B_0 \quad (13.39)$$

as shown in Fig. 13.16 This gives the resonance frequency

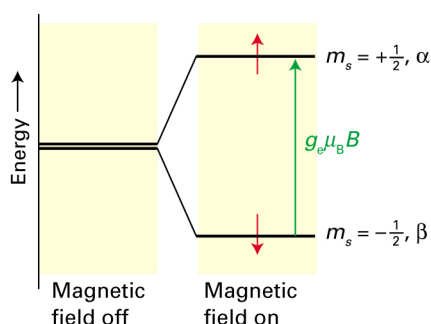


Figure 13.16: The energy gap between the β and α states of the electron in a magnetic field observed in EPR spectroscopy.

$$\nu = \frac{g_e\mu_B}{h}B_0 \quad (13.40)$$

and the relative population difference becomes (cf. Eq. (13.14))

$$\frac{N_\beta - N_\alpha}{N_\beta + N_\alpha} \approx \frac{g_e\mu_B B_0}{2kT} \quad (13.41)$$

at thermal equilibrium.

Exercise 13.11 Verify that at $B_0 = 1$ T and $T = 300$ K, the relative population difference is

$$\frac{N_\beta - N_\alpha}{N_\beta + N_\alpha} \approx 0.2\%$$

Compare this value with the population difference in Exercise 13.3 for the proton. ■

As in NMR spectroscopy, the EPR resonance frequency changes depending on the environment of the electron. Whereas the shielding constant σ is introduced to capture this effect in NMR spectroscopy, the procedure in EPR spectroscopy is to allow the electron g -value to change from its vacuum value $g_e = 2.0023$. The resonance frequency for an unpaired electron in a molecule (radical) thus becomes

$$\nu = \frac{g\mu_B}{h}B_0 \quad (13.42)$$

In organic radicals, the electron g -value changes very little from its vacuum value:

$$g \approx 2.0027 \quad \text{organic radicals}$$

whereas greater changes are observed for inorganic radicals and paramagnetic d-metal complexes:

$$\begin{array}{ll} g \approx 1.9\text{--}2.1 & \text{inorganic radicals} \\ g \approx 0\text{--}6 & \text{d-metal complexes} \end{array}$$

The electron g -value can be computed from electronic-structure wave functions (e.g., Hartree-Fock theory, Kohn-Sham DFT, coupled-cluster theory, etc.) and is mostly used for identification of compounds in practice.

In EPR experiments, the magnetic field is varied and the radiation frequency is kept constant. Moreover, the *derivative* of the absorption intensity with respect to the magnetic field strength is reported. This implies that the absorption maximum is located where the derivative is zero, see Fig. 13.17.

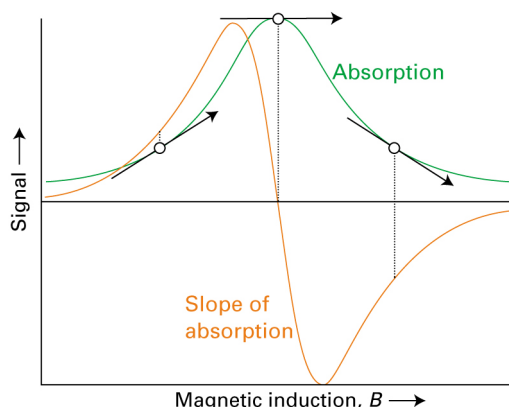


Figure 13.17: The derivative of the absorption intensity is used in EPR spectroscopy instead of the intensity itself.

The EPR spectrum of the benzene anion, C_6H_6^- , in solution is shown in Fig. 13.18. Instead

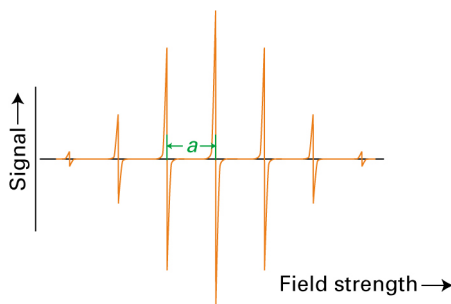


Figure 13.18: EPR spectrum of the benzene anion in solution.

of a single signal, it consists of seven peaks centered around the electron g -value for the anion, with all neighboring peaks separated by the same number a , the *hyperfine coupling constant*. This splitting of the single electronic resonance is called the *hyperfine structure* of the EPR spectrum and is caused by interactions between the electron magnetic moment and nuclear magnetic moments.

In the benzene anion, it is the proton magnetic moments that couple with the electrons—the most abundant carbon isotope is ^{12}C , which is a spin-0 boson and, hence, does not possess a magnetic moment. Protons are fermions with spin $\frac{1}{2}$ and thus gives rise to a magnetic moment. The magnetic moment, in turn, generates a magnetic field which adds to the externally externally

applied field, creating a local magnetic field given by

$$B_{\text{loc}} = B_0 + am_I, \quad m_I = \pm \frac{1}{2} \quad (13.43)$$

where a is the hyperfine coupling constant (for the proton). Even in the presence of an external magnetic field, there are very nearly the same amount of protons in the spin-up state ($m_I = \frac{1}{2}$) as there are protons in the spin-down state ($m_I = -\frac{1}{2}$) in a sample of benzene anions (cf. Exercise 13.3). Hence, coupling to one proton, the electron resonance will be split in two:

$$\nu = \frac{g\mu_B}{h}(B_0 \pm \frac{1}{2}a) \implies B = \frac{h\nu}{g\mu_B} \pm \frac{1}{2}a \quad (13.44)$$

which are separated by a on the magnetic-field axis. Since there are 6 equivalent protons in the benzene anion, the resonance is split into 7 resonances with the intensity ratio 1:6:15:20:15:6:1, as can be verified by application of Pascal's triangle, Fig. 13.11.

In general, coupling with N equivalent nuclei with spin I gives

$$2NI + 1 \text{ lines} \quad \text{coupling with } N \text{ equivalent spin-}I \text{ nuclei} \quad (13.45)$$

The lines are separated by the hyperfine coupling constant, which differs for each type of nucleus. For example, consider a radical with 3 equivalent ^{14}N nuclei. The ^{14}N nucleus has spin $I = 1$, implying that the EPR signal will be split in $2NI + 1 = 2 \times 3 \times 1 + 1 = 7$ lines. The intensity ratio of the lines is 1:3:6:7:6:3:1, as shown in Fig. 13.19. Of course, there may be more than one set of

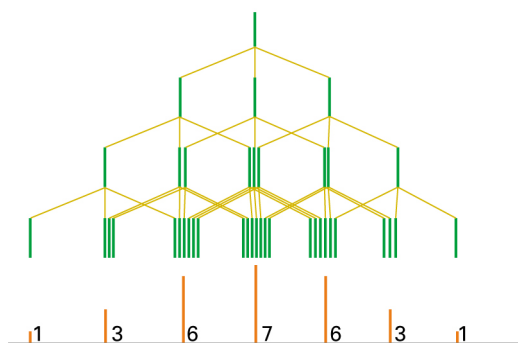


Figure 13.19: EPR hyperfine structure of a radical with three equivalent ^{14}N nuclei.

equivalent magnetic nuclei that couple with the electron magnetic moment. Figure 13.20 shows how a triplet of triplets arises from coupling with one ^{14}N nucleus and two protons. The hyperfine coupling constants are $a = 1.61 \text{ mT}$ for ^{14}N and $a = 0.35 \text{ mT}$ for the protons.

Exercise 13.12 Predict the hyperfine structure of the EPR spectrum of a radical with 2 ^{14}N nuclei and 1 proton. ■

Exercise 13.13 The EPR spectrum of a radical with a single magnetic nucleus is split into four lines of equal intensity. What is the spin of the magnetic nucleus? ■

Exercise 13.14 Sketch the form of the hyperfine structures of radicals XH_2 and XD_2 , where the nucleus X has spin $I = \frac{5}{2}$. ■

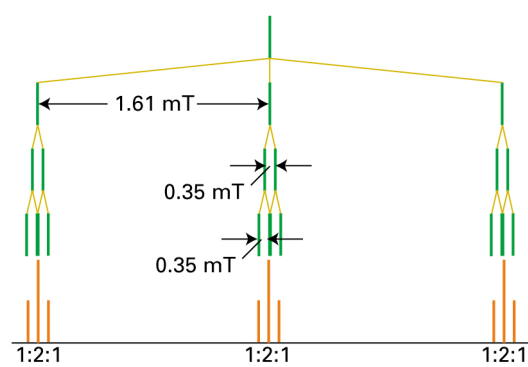


Figure 13.20: EPR hyperfine structure of a radical with one ^{14}N nucleus and two protons.