

UNIT – I  
Electronic Spectroscopy and  
NMR

## Born-Oppenheimer Approximation

The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions.

This involves the following assumptions:

- The electronic wave function depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
- The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.

We know that if a Hamiltonian is separable into two or more terms, then the total eigen functions are products of the individual eigen functions of the separated Hamiltonian terms, and the total eigen values are sums of individual eigen values of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian which is separable into two terms, one involving coordinate  $q_1$  and the other involving coordinate  $q_2$ .

$$H = H_1(q_1) + H_2(q_2)$$

With the overall Schrödinger equation being

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wavefunction can be written in the form  $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$  where  $\psi_1(q_1)$  and  $\psi_2(q_2)$  are eigen functions of  $H_1$  and  $H_2$  with eigenvalues  $E_1$  and  $E_2$ , then

$$H\psi(q_1, q_2) =$$

$$=$$

Thus the products of the  $H_1$  and  $H_2$ , and the eigenvalues of  $H_1$  and  $H_2$  are eigenfunctions of  $H_1$  and  $H_2$ . The eigenvalues are the sums  $E_1 + E_2$  and  $E$ .

$$= (H_1 + H_2)\psi_1(q_1)\psi_2(q_2)$$

$$= H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2)$$

$$= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2)$$

$$(E_1 + E_2)\psi_1(q_1)\psi_2(q_2)$$

$$E\psi(q_1, q_2)$$

Going back to our original problem, we would start by seeking the eigenfunctions and eigenvalues of this Hamiltonian, which will be given by solution of the time-independent Schrödinger equation

$$[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})] \Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}).$$

We first invoke the Born-Oppenheimer approximation by recognizing that, in a dynamical sense, there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be exploited by assuming a quasi-separable ansatz of the form

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi_e(\mathbf{x}, \mathbf{R})\phi_N(\mathbf{R})$$

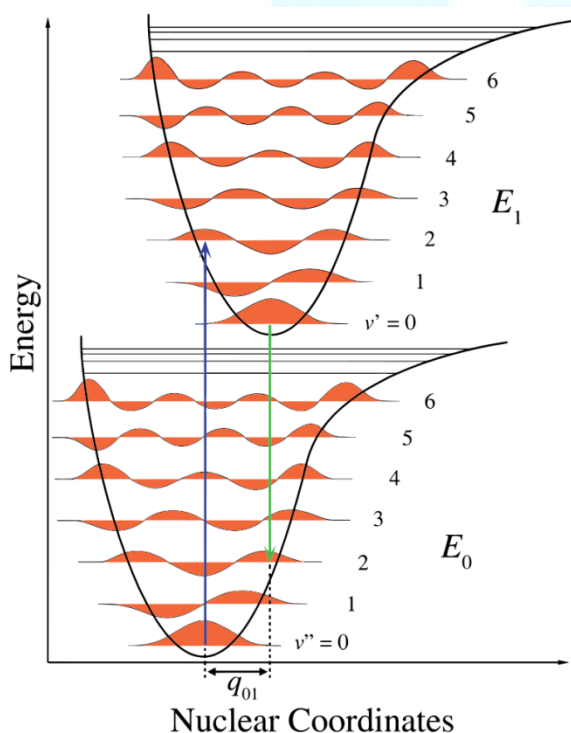
where  $\phi_N(\mathbf{R})$  is a nuclear wave function and  $\phi_e(\mathbf{x}, \mathbf{R})$  is an electronic wave function that depends parametrically on the nuclear positions. If we look again at the Hamiltonian, we would notice right away that the term  $V_{eN}$  would prevent us from applying this separation of variables. The Born-Oppenheimer (named for its original inventors, Max Born and Robert Oppenheimer) is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. In a dynamical sense, the electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are "dragged" along with the nuclei without requiring a finite relaxation time. This, of course, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this "instantaneous" manner, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.

## Franck–Condon principle

The **Franck–Condon principle** is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.

Electronic transitions are relatively instantaneous compared with the time scale of nuclear motions, therefore if the molecule is to move to a new vibrational level during the electronic transition, this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state. In the semiclassical picture of vibrations (oscillations) of a simple harmonic oscillator, the necessary conditions can occur at the turning points, where the momentum is zero.

Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck–Condon state, and the transition involved, a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.



Rotational fine structure of electronic Vibrational Transstion

Electronic transitions are typically observed in the visible and ultraviolet regions, in the wavelength range approximately 200–700 nm (50,000–14,000 cm<sup>-1</sup>), whereas fundamental vibrations are observed below about 4000 cm<sup>-1</sup>.<sup>[note 1]</sup> When the electronic and vibrational energy changes are so different, vibronic coupling (mixing of electronic and vibrational wave functions) can be neglected and the energy of a vibronic level can be taken as the sum of the electronic and vibrational (and rotational) energies; that is, the Born–Oppenheimer approximation applies.<sup>[4]</sup> The overall molecular energy depends not only on the electronic state but also on vibrational and rotational quantum numbers, denoted  $v$  and  $J$  respectively for diatomic molecules. It is conventional to add a double prime ( $v''$ ,  $J''$ ) for levels of the electronic ground state and a single prime ( $v'$ ,  $J'$ ) for electronically excited states.

Each electronic transition may show vibrational coarse structure, and for molecules in the gas phase, rotational fine structure. This is true even when the molecule has a zero dipole moment and therefore has no vibration-rotation infrared spectrum or pure rotational microwave spectrum.<sup>[5]</sup>

It is necessary to distinguish between absorption and emission spectra. With absorption the molecule starts in the ground electronic state, and usually also in the vibrational ground state because at ordinary temperatures the energy necessary for vibrational excitation is large compared to the average thermal energy. The molecule is excited to

another electronic state and to many possible vibrational states. With emission, the molecule can start in various populated vibrational states, and finishes in the electronic ground state in one of many populated vibrational levels. The emission spectrum is more complicated than the absorption spectrum of the same molecule because there are more changes in vibrational energy level.

For absorption spectra, the vibrational coarse structure for a given electronic transition forms single *progression*, or series of transitions with a common level, here the lower

level. There are no selection rules for vibrational quantum numbers, which are zero in the ground vibrational level of the initial electronic ground state, but can take any integer values in the final electronic excited state. The term values  $G(v)$  for a harmonic oscillator are given by

$$G(v) = \nu_{\text{electronic}} + \nu_e(v+1/2)$$

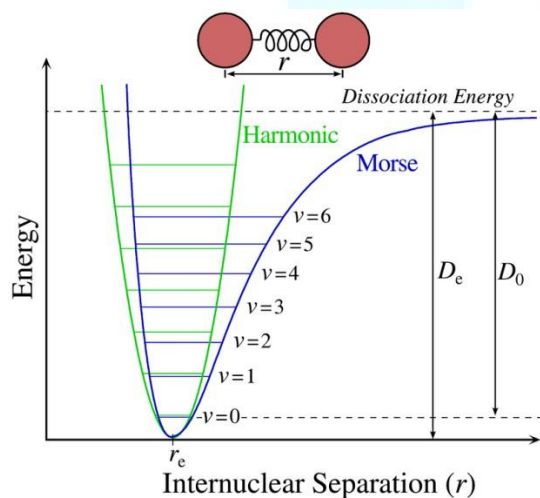
where  $v$  is a vibrational quantum number,  $\omega_e$  is the harmonic wavenumber. In the next approximation the term values are given by

$$G(v) = G_{\text{electronic}} + G_e(v+1/2) - \chi_e G_e(v+1/2)^2$$

where  $\chi_e$  is an anharmonicity constant. This is, in effect, a better approximation to the Morse potential near the potential minimum. The spacing between adjacent vibrational lines decreases with increasing quantum number because of anharmonicity in the vibration. Eventually the separation decreases to zero when the molecule photo-dissociates into a continuum of states. The second formula is adequate for small values of the vibrational quantum number. For higher values further anharmonicity terms are needed as the molecule approaches the dissociation limit, at the energy corresponding to the upper (final state) potential curve at infinite internuclear distance.

The intensity of allowed vibronic transitions is governed by the Franck–Condon principle.<sup>[7]</sup> Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates, that is, when the transition is "vertical" on the energy level diagram. Each line has a finite linewidth, dependent on a variety of factors.<sup>[8]</sup>

Vibronic spectra of diatomic molecules in the gas phase have been analyzed in detail.<sup>[9]</sup> Vibrational coarse structure can sometimes be observed in the spectra of molecules in liquid or solid phases and of molecules in solution. Related phenomena including photoelectron spectroscopy, resonance Raman spectroscopy, luminescence, and fluorescence are not discussed in this article, though they also involve vibronic transitions.



The **Morse potential** (blue) and harmonic oscillator potential (green). The potential at infinite internuclear distance is the dissociation energy for pure vibrational spectra. For vibronic spectra there are two potential curves

## NMR

**Nuclear magnetic resonance (NMR)** is a physical phenomenon in which nuclei in a strong constant magnetic field are perturbed by a weak oscillating magnetic field (in the near field<sup>[11]</sup>) and respond by producing an electromagnetic signal with a frequency

characteristic of the magnetic field at the nucleus. This process occurs near resonance, when the oscillation frequency matches the intrinsic frequency of the nuclei, which depends on the strength of the static magnetic field, the chemical environment, and the magnetic properties of the isotope involved; in practical applications with static magnetic fields up to ca. 20 tesla, the frequency is similar to VHF and UHF television broadcasts (60–1000 MHz). NMR results from specific magnetic properties of certain atomic nuclei. Nuclear magnetic resonance spectroscopy is widely used to determine the structure of organic molecules in solution and study molecular physics and crystals as well as non-crystalline materials. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

All isotopes that contain an odd number of protons and/or neutrons (see Isotope) have an intrinsic nuclear magnetic moment and angular momentum, in other words a nonzero nuclear spin, while all nuclides with even numbers of both have a total spin of zero. The most commonly used nuclei are  $^1\text{H}$  and  $^{13}\text{C}$ , although isotopes of many other elements can be studied by high-field NMR spectroscopy as well.

A key feature of NMR is that the resonance frequency of a particular sample substance is usually directly proportional to the strength of the applied magnetic field. It is this feature that is exploited in imaging techniques; if a sample is placed in a non-uniform magnetic field then the resonance frequencies of the sample's nuclei depend on where in the field they are located. Since the resolution of the imaging technique depends on the magnitude of the magnetic field gradient, many efforts are made to develop increased gradient field strength.

The principle of NMR usually involves three sequential steps:

- The alignment (polarization) of the magnetic nuclear spins in an applied, constant magnetic field  $\mathbf{B}_0$ .
- The perturbation of this alignment of the nuclear spins by a weak oscillating magnetic field, usually referred to as a radio-frequency (RF) pulse. The oscillation frequency required for significant perturbation is dependent upon the static magnetic field ( $\mathbf{B}_0$ ) and the nuclei of observation.
- The detection of the NMR signal during or after the RF pulse, due to the voltage induced in a detection coil by precession of the nuclear spins around  $\mathbf{B}_0$ . After an RF pulse, precession usually occurs with the nuclei's intrinsic Larmor frequency and, in itself, does not involve transitions between spin states or energy levels.<sup>[1]</sup>

The two magnetic fields are usually chosen to be perpendicular to each other as this maximizes the NMR signal strength. The frequencies of the time-signal response by the total magnetization ( $\mathbf{M}$ ) of the nuclear spins are analyzed in NMR spectroscopy and magnetic resonance imaging. Both use applied magnetic fields ( $\mathbf{B}_0$ ) of great strength, often produced by large currents in superconducting coils, in order to achieve dispersion of response frequencies and of very high homogeneity and stability in order to deliver spectral

resolution, the details of which are described by chemical shifts, the Zeeman effect, and Knight shifts (in metals). The information provided by NMR can also be increased using hyperpolarization, and/or using two-dimensional, threedimensional and higher-dimensional techniques.

NMR phenomena are also utilized in low-field NMR, NMR spectroscopy and MRI in the Earth's magnetic field (referred to as Earth's field NMR), and in several types of magnetometers.

### **Nuclear spin and magnets**

All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin, an intrinsic angular momentum analogous to the classical angular momentum of a spinning sphere. The overall spin of the nucleus is determined by the spin quantum number  $S$ . If the numbers of both the protons and neutrons in a given nuclide are even then  $S = 0$ , i.e. there is no overall spin. Then, just as electrons pair up in non degenerate atomic orbitals, so do even numbers of protons or

even numbers of neutrons (both of which are also spin particles and hence fermions), giving zero overall spin.

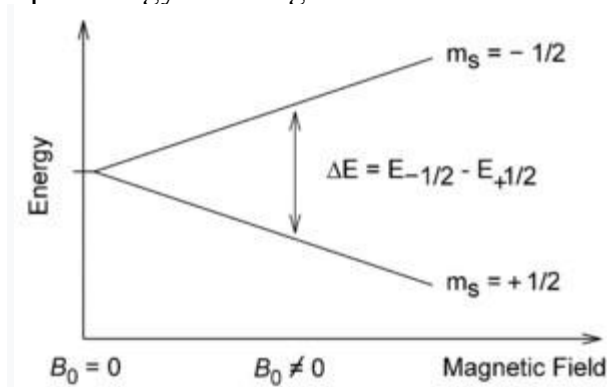
However, a proton and neutron will have lower energy when their spins are parallel, not anti-parallel. This parallel spin alignment of distinguishable particles does not violate the Pauli exclusion principle. The lowering of energy for parallel spins has to do with the quark structure of these two nucleons. As a result, the spin ground state for the deuteron (the nucleus of deuterium, the  $^2\text{H}$  isotope of hydrogen), which has only a proton and a neutron, corresponds to a spin value of **1**, *not of zero*. On the other hand, because of the Pauli exclusion principle, the tritium isotope of hydrogen must have a pair of antiparallel spin neutrons (of total spin zero for the neutron-spin pair), plus a proton of spin  $1/2$ . Therefore, the tritium total nuclear spin value is again  $1/2$ , just like for the simpler, abundant hydrogen isotope,  $^1\text{H}$  nucleus (the *proton*). The NMR absorption frequency for tritium is also similar to that of  $^1\text{H}$ . In many other cases of *nonradioactive* nuclei, the overall spin is also non-zero. For example, the  $^{27}\text{Al}$  nucleus has an overall spin value  $S = 5/2$ .

Classically, this corresponds to the proportionality between the angular momentum and the magnetic dipole moment of a spinning charged sphere, both of which are vectors parallel to the rotation axis whose length increases proportional to the spinning frequency. It is the magnetic moment and its interaction with magnetic fields that allows the observation of NMR signal associated with transitions between nuclear spin levels during resonant RF irradiation or caused by Larmor precession of the average magnetic moment after resonant irradiation. Nuclides with even numbers of both protons and neutrons have zero nuclear magnetic dipole moment and hence do not exhibit NMR signal. For instance,  $^{18}\text{O}$  is an example of a nuclide that produces no NMR signal, whereas  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  are nuclides that do exhibit NMR spectra. The last two nuclei have spin  $S > 1/2$  and are therefore quadrupolar nuclei. **Values of spin angular momentum**



Nuclear spin is an intrinsic angular momentum that is quantized. This means that the magnitude of this angular momentum is quantized (i.e.  $S$  can only take on a restricted range of values), and also that the x, y, and z-components of the angular momentum are quantized, being restricted to integer or half-integer multiples of  $\hbar$ . The integer or halfinteger quantum number associated with the spin component along the z-axis or the applied magnetic field is known as the magnetic quantum number,  $m$ , and can take values from  $+S$  to  $-S$ , in integer steps. Hence for any given nucleus, there are a total of  $2S + 1$  angular momentum states.

Spin energy in a magnetic field



Splitting of nuclei spin energies in an external magnetic field Consider nuclei with a spin of one-half, like  $^1\text{H}$ ,  $^{13}\text{C}$  or  $^{19}\text{F}$

Each nucleus has two linearly independent spin states, with  $m = 1/2$  or  $m = -1/2$  (also referred to as spin-up and spin-down, or sometimes  $\alpha$  and  $\beta$  spin states, respectively) for the z-component of spin. In the absence of a magnetic field, these states are degenerate; that is, they have the same energy. Hence the number of nuclei in these two states will be essentially equal at thermal equilibrium.

### Relaxation Process

The process of population relaxation refers to nuclear spins that return to thermodynamic equilibrium in the magnet. This process is also called  $T_1$ , "spin-lattice" or "longitudinal magnetic" relaxation, where  $T_1$  refers to the mean time for an individual nucleus to return to its thermal equilibrium state of the spins. After the nuclear spin population has relaxed, it can be probed again, since it is in the initial, equilibrium (mixed) state.

The precessing nuclei can also fall out of alignment with each other and gradually stop producing a signal. This is called  $T_2$  or *transverse relaxation*. Because of the difference in the actual relaxation mechanisms involved (for example, intermolecular versus intramolecular magnetic dipole-dipole interactions),  $T_1$  is usually (except in rare cases) longer than  $T_2$  (that is, slower spin-lattice relaxation, for example because of smaller dipole-dipole interaction effects). In practice, the value of  $T_2^*$  which is the actually observed decay time of the observed NMR signal, or free induction decay (to  $1/e$  of the

initial amplitude immediately after the resonant RF pulse), also depends on the static magnetic field inhomogeneity, which is quite significant. (There is also a smaller but significant contribution to the observed FID shortening from the RF inhomogeneity of the resonant pulse).<sup>[citation needed]</sup> In the corresponding FT-NMR spectrum—meaning the Fourier transform of the free induction decay—the  $T_2^*$  time is inversely related to the width of the NMR signal in frequency units. Thus, a nucleus with a long  $T_2$  relaxation time gives rise to a very sharp NMR peak in the FT-NMR spectrum for a very homogeneous ("well-shimmed") static magnetic field, whereas nuclei with shorter  $T_2$  values give rise to broad FT-NMR peaks even when the magnet is shimmed well. Both  $T_1$  and  $T_2$  depend on the rate of molecular motions as well as the gyromagnetic ratios of both the resonating and their strongly interacting, next-neighbor nuclei that are not at resonance.

### Fourier-transform spectroscopy

Most applications of NMR involve full NMR spectra, that is, the intensity of the NMR signal as a function of frequency. Early attempts to acquire the NMR spectrum more efficiently than simple CW methods involved illuminating the target simultaneously with more than one frequency. A revolution in NMR occurred when short radio-frequency pulses began to be used, with a frequency centered at the middle of the NMR spectrum. In simple terms, a short pulse of a given "carrier" frequency "contains" a range of frequencies centered about the carrier frequency, with the range of excitation (bandwidth) being inversely proportional to the pulse duration, i.e. the Fourier transform of a short pulse contains contributions from all the frequencies in the neighborhood of the principal frequency.<sup>[16]</sup> The restricted range of the NMR frequencies made it relatively easy to use short (1 - 100 microsecond) radio frequency pulses to excite the entire NMR spectrum.

Applying such a pulse to a set of nuclear spins simultaneously excites all the single-quantum NMR transitions. In terms of the net magnetization vector, this corresponds to tilting the magnetization vector away from its equilibrium position (aligned along the external magnetic field). The out-of-equilibrium magnetization vector then precesses about the external magnetic field vector at the NMR frequency of the spins. This oscillating magnetization vector induces a voltage in a nearby pickup coil, creating an electrical signal oscillating at the NMR frequency. This signal is known as the free induction decay (FID), and it contains the sum of the NMR responses from all the excited spins. In order to obtain the frequency-domain NMR spectrum (NMR absorption intensity vs. NMR frequency) this time-domain signal (intensity vs. time) must be Fourier transformed. Fortunately, the development of Fourier transform (FT) NMR coincided with the development of digital computers and the digital Fast Fourier Transform. Fourier methods can be applied to many types of spectroscopy. (See the full article on Fourier transform spectroscopy.)

## <sup>13</sup>C NMR Spectroscopy

**Carbon-13 (C13) nuclear magnetic resonance** (most commonly known as **carbon-13 NMR** or <sup>13</sup>C NMR or sometimes simply referred to as **carbon NMR**) is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is analogous to proton NMR (<sup>1</sup>H NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such <sup>13</sup>C NMR is an important tool in chemical structure elucidation in organic chemistry <sup>13</sup>C NMR detects only the <sup>13</sup>C isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope, <sup>12</sup>C, is not detectable by NMR since its nucleus has zero spin.

reagents,<sup>[3]</sup> for example Cr(acac)<sub>3</sub> (chromium(III) acetylacetonate), and appropriate pulse sequences have reduced the time needed to acquire quantitative spectra and have made quantitative carbon-13 NMR a commonly used technique in many industrial labs. Applications range from quantification of drug purity to determination of the composition of high molecular weight synthetic polymers.

In a typical run on an organic compound, a <sup>13</sup>C NMR may require several hours to record the spectrum of a one-milligram sample, compared to 15–30 minutes for <sup>1</sup>H NMR, and that spectrum would be of lower quality. The nuclear dipole is weaker, the difference in energy between alpha and beta states is one-quarter that of proton NMR, and the Boltzmann population difference is correspondingly less.

### Chemical Shift

In nuclear magnetic resonance (NMR) spectroscopy, the **chemical shift** is the resonant frequency of a nucleus relative to a standard in a magnetic field. Often the position and number of chemical shifts are diagnostic of the structure of a molecule. Chemical shifts are also used to describe signals in other forms of spectroscopy such as photoemission spectroscopy.

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<sup>13</sup>C NMR has a number of complications that are not encountered in proton NMR. <sup>13</sup>C NMR is much less sensitive to carbon than <sup>1</sup>H NMR is to hydrogen since the major isotope of carbon, the <sup>12</sup>C isotope, has a spin quantum number of zero and so is not magnetically active and therefore not detectable by NMR. Only the much less common <sup>13</sup>C isotope, present naturally at 1.1% natural abundance, is magnetically active with a spin quantum number of 1/2 (like <sup>1</sup>H) and therefore detectable by NMR. Therefore, only the few <sup>13</sup>C nuclei present resonate in the magnetic field, although this can be overcome by isotopic enrichment of e.g. protein samples. In addition, the gyromagnetic ratio (6.728284 10<sup>7</sup> rad T<sup>-1</sup> s<sup>-1</sup>) is only 1/4 that of <sup>1</sup>H, further reducing the sensitivity. The overall *receptivity* of <sup>13</sup>C is about 4 orders of magnitude lower than <sup>1</sup>H.

High field magnets with internal bores capable of accepting larger sample tubes (typically 10 mm in diameter for <sup>13</sup>C NMR versus 5 mm for <sup>1</sup>H NMR), the use of relaxation

Some atomic nuclei possess a magnetic moment (nuclear spin), which gives rise to different energy levels and resonance frequencies in a magnetic field. The total magnetic field experienced by a nucleus includes local magnetic fields induced by currents of electrons in the molecular orbitals (note that electrons have a magnetic moment themselves). The electron distribution of the same type of nucleus (e.g.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) usually varies according to the local geometry (binding partners, bond lengths, angles between bonds, and so on), and with it the local magnetic field at each nucleus. This is reflected in the spin energy levels (and resonance frequencies). The variations of nuclear magnetic resonance frequencies of the same kind of nucleus, due to variations in the electron distribution, is called the chemical shift. The size of the chemical shift is given with respect to a reference frequency or reference sample (see also chemical shift referencing), usually a molecule with a barely distorted electron distribution.

### Spin- Spin Coupling

In addition to chemical shift, NMR spectra allow structural assignments by virtue of spin <https://en.wikipedia.org/wiki/Carbon-13> spin coupling (and integrated intensities). Because nuclei themselves possess a small magnetic field, they influence each other, changing the energy and hence frequency of nearby nuclei as they resonate—this is known as spin-spin coupling. The most important type in basic NMR is *scalar coupling*. This interaction between two nuclei occurs through chemical bonds, and can typically be seen up to three bonds away (3-J coupling), although it can occasionally be visible over four to five bonds, though these tend to be considerably weaker. The effect of scalar coupling can be understood by examination of a proton which has a signal at 1 ppm. This proton is in a hypothetical molecule where three bonds away exists another proton (in a CH-CH group for instance), the neighbouring group (a magnetic field) causes the signal at 1 ppm to split into two, with one peak being a few hertz higher than 1 ppm and the other peak being the same number of hertz lower than 1 ppm. These peaks each have half the area of the former **singlet** peak. The magnitude of this splitting (difference in frequency between peaks) is known as the coupling constant. A typical coupling constant value for aliphatic protons would be 7 Hz.

The coupling constant is independent of magnetic field strength because it is caused by the magnetic field of another nucleus, not the spectrometer magnet. Therefore, it is quoted in hertz (frequency) and not ppm (chemical shift).

In another molecule a proton resonates at 2.5 ppm and that proton would also be split into two by the proton at 1 ppm. Because the magnitude of interaction is the same the splitting would have the same coupling constant 7 Hz apart. The spectrum would have two signals, each being a **doublet**. Each doublet will have the same area because both doublets are produced by one proton each.

The two doublets at 1 ppm and 2.5 ppm from the fictional molecule CH-CH are now changed into CH<sub>2</sub>-CH:

- The total area of the 1 ppm CH<sub>2</sub> peak will be twice that of the 2.5 ppm CH peak.
- The CH<sub>2</sub> peak will be split into a doublet by the CH peak—with one peak at 1 ppm + 3.5 Hz and one at 1 ppm - 3.5 Hz (total splitting or coupling constant is 7 Hz).

In consequence the CH peak at 2.5 ppm will be split *twice* by each proton from the CH<sub>2</sub>. The first proton will split the peak into two equal intensities and will go from one peak at 2.5 ppm to two peaks, one at 2.5 ppm + 3.5 Hz and the other at 2.5 ppm - 3.5 Hz—each having equal intensities. However these will be split again by the second proton. The frequencies will change accordingly:

- The 2.5 ppm + 3.5 Hz signal will be split into 2.5 ppm + 7 Hz and 2.5 ppm
- The 2.5 ppm - 3.5 Hz signal will be split into 2.5 ppm and 2.5 ppm - 7 Hz

The net result is not a signal consisting of 4 peaks but three: one signal at 7 Hz above 2.5 ppm, two signals occur at 2.5 ppm, and a final one at 7 Hz below 2.5 ppm. The ratio of height between them is 1:2:1. This is known as a **triplet** and is an indicator that the proton is three-bonds from a CH<sub>2</sub> group.

This can be extended to any CH<sub>n</sub> group. When the CH<sub>2</sub>-CH group is changed to CH<sub>3</sub><https://en.wikipedia.org/wiki/Carbon-13>CH<sub>2</sub>, keeping the chemical shift and coupling constants identical, the following changes are observed:

- The relative areas between the CH<sub>3</sub> and CH<sub>2</sub> subunits will be 3:2.
- The CH<sub>3</sub> is coupled to two protons into a 1:2:1 **triplet** around 1 ppm.
- The CH<sub>2</sub> is coupled to *three* protons.

