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## **Theory of spin magnetic resonance: derivations of energy spacing and chemical shifts in NMR spectroscopy.**

### **Introduction**

The simplicity of a spin  $1/2$  particle in a time dependent electromagnetic potential makes it possible to develop an exact solution, which is always very useful in theoretical analysis and which makes it particularly well suited to introducing time-dependent perturbation theory to neophyte graduate students. In addition, since many nuclei possess an overall spin of  $1/2$ , this problem becomes particularly applicable to chemistry and materials science in the form of nuclear magnetic resonance (NMR). This quantum mechanical interaction of the particle with the electromagnetic field allows insight into an atom's gyromagnetic ratio, a parameter particular to each element and isotope. Furthermore, the dependence of effective magnetic field on both the applied magnetic field and the charge environment surrounding the nucleus makes it possible to determine not only atomic and isotopic information, but also the nature of the bonds in molecules. None of this would be possible without a theoretical treatment of the two state harmonic time dependent potential. Eventually, it will be necessary to introduce the details of the nucleus-magnetic field interaction, but to begin we can treat the general problem of a two state system.

### **Basic treatment**

To begin, the time-independent Hamiltonian and the time-dependent perturbation may be described as in Sakurai

$$H = E_1|1\rangle\langle 1| + E_2|2\rangle\langle 2|$$

$$V(t) = \lambda(\exp(i\omega t)|1\rangle\langle 2| + \exp(-i\omega t)|2\rangle\langle 1|)$$

The solution takes the form of

$$c_1(t)|1\rangle + c_2(t)|2\rangle$$

At  $t=0$ , assume  $c_1(0) = 1$ ,  $c_2(0) = 0$ . The coupled differential equation

$$i \hbar \frac{dc_1}{dt} = \lambda \exp(i(\omega - \omega_{12})t)c_2 \quad i \hbar \frac{dc_2}{dt} = \lambda \exp(-i(\omega - \omega_{12})t)c_1$$

with

$$\omega_{12} = (E_2 - E_1)/\hbar$$

may be solved as follows. A differentiation and substitution takes the equations to the form

$$d^2c_2/dt^2 = -(\lambda/\hbar)^2 c_2 - i(\omega - \omega_{12}) dc_2/dt$$

From which we see that that

$$c_2(t) = \exp(-i(\omega - \omega_{12})t/2) A \sin(\Omega t)$$

with

$$\Omega = ((\lambda/\hbar)^2 + (\omega - \omega_{12})^2/4)^{1/2}$$

and A a constant to be determined. The initial condition then gives  $A = \gamma/\hbar\Omega$ , and since the phase factor  $\exp(-i(\omega - \omega_{12})t/2)$  cancels in the modulus of  $c_2(t)$

$$|c_2(t)|^2 = (\lambda/\hbar\Omega)^2 \sin^2(\Omega t)$$

This result is called Rabi's formula

$$|c_2(t)|^2 = (\lambda/\hbar)^2 / ((\lambda/\hbar)^2 + (\omega - \omega_{12})^2/4) \sin^2(((\lambda/\hbar)^2 + (\omega - \omega_{12})^2/4)^{1/2} t)$$

A similar calculation shows

$$|c_1(t)|^2 = 1 - |c_2(t)|^2$$

which should be the case due to the unitarity of both  $H_0$  and  $V(t)$ .

### **Applicability to Nuclear Magnetic Resonance**

We will now focus on the case of nuclei possessing spin  $1/2$ , though with some modification this can be connected with electron spin such as in EPR as well. The use of a spin  $1/2$  system is important since integer spin allows the possibility of  $S_z = 0$ , which precludes any nuclear magnetic moment.

In terms of the specific problem of NMR, the time independent and time dependent components of the Hamiltonian, are outgrowths of the interaction between nuclear spin magnetic moment and externally applied magnetic fields.

$$\mathbf{B} = B_0 \mathbf{z} + B_1 (\mathbf{x} \cos(\omega t) + \mathbf{y} \sin(\omega t))$$

$$\boldsymbol{\mu} = \gamma \mathbf{S}$$

where  $\gamma$  is the gyromagnetic ratio and  $\mathbf{S}$  is the spin moment, which, in the basis of the unperturbed system aligned with  $\mathbf{z}$ , has eigenvalues of  $+\hbar/2$  or  $-\hbar/2$ . The Hamiltonian and perturbation which arise from this are

$$H_0 = (\gamma \hbar B_0/2)(|+\rangle\langle+| - |-\rangle\langle-|)$$

$$V(t) = -(\gamma \hbar B_1/2)(\exp(i \omega t)|+\rangle\langle-| + \exp(-i \omega t)|-\rangle\langle+|)$$

where  $|+\rangle$ , and  $|-\rangle$  represent the states with their magnetic moments aligned and anti-aligned with the magnetic field. In the absence of any perturbation, according to Boltzmann statistics at equilibrium, there will be a preference for the lower energy state,  $|+\rangle$ , as  $\exp(-\Delta E/k_b T)$ . Although this preference is small at room temperature (e.g. for every  $10^6$  protons, there is only one extra aligned with the magnetic field), it is reasonable to treat this surplus as the signal to be detected in experiments and disregard the background populations whose spins anti-align and effectively cancel out. Therefore, the problem can be treated as if a nucleus has already relaxed to the ground state pointing in the direction of the magnetic field. That is for our state at the beginning of the perturbation

$$|\alpha\rangle = c_+(0)|+\rangle + c_-(0)|-\rangle$$

we may treat it as if each nucleus that matters has relaxed to the ground state  $|+\rangle$ , i.e.  $c_-(0) = 0$ .

From this we can see the obvious correspondence to the previous treatment of the generic two state problem.  $E_1$  and  $E_2$  correspond to the energy associated with the eigenstates aligned and anti-aligned with the constant magnetic field  $B_0$ . The form of Rabi's formula is then given by

$$|c_-(t)|^2 = (\gamma B_1/2)^2 / ((\gamma B_1/2)^2 + (\omega - \omega_{12})^2/4) \sin^2(((\gamma B_1/2)^2 + (\omega - \omega_{12})^2/4)^{1/2} t)$$

with the resonance frequency given by

$$\omega_{12} = \gamma B_0$$

This is recognizable as the Larmor frequency of precession about the axis of the magnetic field  $B_0$  for a state composed of a linear combination of energy eigenstates  $|+\rangle$  and  $|-\rangle$  in the absence of the perturbing field. From the  $\sin^2$  term, we see that the nuclear spin flips from  $|+\rangle$  to  $|-\rangle$  periodically as the incident radiation provides excess energy to drive this transition. Additionally, it can be seen that the magnitude of the coefficient  $c_2(t)$  contains the term  $\omega - \omega_{12}$  in the denominator, (i.e. the maximum value of  $|c_2|^2$  is less than 1 if  $\omega$  is not equal to  $\omega_{12}$ ). The transfer from the low to the high energy state is accomplished by the absorption and reemission of rf radiation. By measuring the intensity of the radiation passing through the sample one can effectively determine which state the sample is in. Thus, the energy difference  $\hbar \omega_{12}$  can be computed by scanning a range of  $\omega$  values and finding the one which maximizes the absorption and reemission magnitude. Contrarily, one could also fix the value of the rf frequency  $\omega$  and

vary the applied magnetic field  $B_0$ . Either way, by a combination of  $B_0$  and  $\omega$  which maximizes the signal, it is then possible to determine the gyromagnetic ratio

$$\gamma = (e/2m_p)g,$$

which is a fundamental and unique characteristic of a given nucleus. This method consisting of scanning frequency or magnetic field and detecting a maximum is referred to as continuous wave NMR, which was the most widely used until the 1970s when Fourier transform (FT) instruments became available. Although FT-NMR is conventionally described in a classical analogy with the rotation of a magnetization vector away from the z-axis, it is possible to explain it with the quantum mechanical formalism of a finite duration harmonic perturbation along with the time evolution of the Schrodinger equation.

### FT-NMR

As every experimental measurement contains some noisiness, it is often desirable to perform repeated experiments to correctly discern signal, which grows linearly with number of measurements, from noise, which grows as the square root. However, utilizing continuous wave NMR, averaging enough data can take a prohibitively long time. To prevent the need to scan each frequency in the spectrum one-by-one FT-NMR uses a short pulse of rf, which has a Fourier transform composed of all frequencies within a bandwidth proportional to the inverse of the pulse duration. Because only the radiation at the resonant frequency can contribute significantly to the conversion between  $|+\rangle$  and  $|-\rangle$  eigenstates, the wide range of emitted frequencies far from resonance aren't important. In fact, this property was already taken advantage of in the continuous wave case for practical purposes. In actuality, it turns out to be rather difficult to produce a circularly oscillating magnetic field so a field oscillating orthogonal to the z axis is used instead. This linearly polarized magnetic field can be decomposed into two circularly polarized fields

$$B_1 \cos(\omega t) \mathbf{x} = \frac{1}{2} B_1(\cos(\omega t) \mathbf{x} + \sin(\omega t) \mathbf{y}) + \frac{1}{2} B_1(\cos(\omega t) \mathbf{x} - \sin(\omega t) \mathbf{y})$$

which is to say two fields with opposite  $\omega$ . Therefore, if one of those rotating fields, say  $+\omega$ , is close to the resonant frequency  $\omega_{12}$  the maximum transition amplitude for that field is  $\sim 1$  whereas for  $-\omega \approx -\omega_{12}$  the transition amplitude goes as

$$(\gamma B_1/2mc)^2 / ((\gamma B_1/2mc)^2 + (-2\omega_{12})^2/4) = 1 / (1 + (2mc\omega_{12}/\gamma B_1)^2)$$

which can be kept small for  $B_1$  small. Ultimately, this resonance with the precession frequency for small  $B_1$  is what allows FT-NMR to work.

In the above treatment of the time dependent perturbation, it was assumed that the perturbation was turned on at  $t = 0$ . Now, assume that the perturbation were turned off at some future time point  $t = t_f$ . The spin would be in some state

$$|\alpha; t = t_f\rangle = c_+(t_f)|+\rangle + c_-(t_f)|-\rangle$$

Let us assume that  $t_f$  has been chosen appropriately so that the moduli of each of the coefficients are equal

$$|c_+(t_f)|^2 = |c_-(t_f)|^2 = 1/2.$$

For simplicity, let us assume further that the coefficients themselves,  $c_+(t_f)$  and  $c_-(t_f)$ , are real and positive, which is indicative of the state  $|S_x +\rangle$ . The inclusion of complex coefficients with moduli still equal to  $1/2$  merely rotates the state in the  $\mathbf{x}$ - $\mathbf{y}$  plane and changes the state to some linear combination of  $|S_x \pm\rangle$  and  $|S_y \pm\rangle$ , but since there is no axial asymmetry, we may choose the axes as we have. Therefore, after  $t = t_f$  we have returned to the time independent Hamiltonian in a superposition of energy eigenstates

$$|\alpha; t = t_f\rangle = |S_x +\rangle = 1/\sqrt{2}(|+\rangle + |-\rangle),$$

which shows a time dependence in  $H_0$  of the form

$$|\alpha; t\rangle = 1/\sqrt{2}(\exp(-i\omega_{12}t)|+\rangle + \exp(i\omega_{12}t)|-\rangle)$$

The projection of this new state onto the  $\mathbf{x}$  axis takes the form

$$|\langle S_x + | \alpha; t \rangle|^2 = \cos^2(\omega_{12}t/2), \quad |\langle S_x - | \alpha; t \rangle|^2 = \sin^2(\omega_{12}t/2)$$

From which we can see that the expectation of  $S_x$  varies like

$$\langle S_x \rangle = (\hbar/2)\cos(\omega_{12}t)$$

Now we see the origin of the Larmor precession alluded to earlier. In an eigenstate of  $S_z$  the values of  $\langle S_x \rangle$  and  $\langle S_y \rangle$  are both zero, but when the spin is left in a superposition of eigenstates  $|+\rangle$  and  $|-\rangle$  these expectation values vary sinusoidally in time. This can be, and frequently is, interpreted as a spin vector whose projection onto the  $\mathbf{x}$ - $\mathbf{y}$  plane rotates with the frequency  $\omega_{12}$ . Now, just as in the case when the applied time-dependent magnetic field induced the energy transition from the  $|+\rangle$  to the  $|-\rangle$  states, the precession about the  $\mathbf{z}$  axis looks like an oscillation in the eigenvalue of the  $S_x$  and  $S_y$  operators, which in turn must induce an oscillatory magnetic field of the same frequency. This precession radiation then gives rise to a reemitted signal which is measured by the same coil that functioned as the rf source. So in terms of the actual FT-NMR experiment, the entire procedure consists solely in finding the appropriate  $t_f$ , measuring the corresponding Larmor precession in the time domain, and (as the name suggests) Fourier transforming this output into the frequency domain. Many measurements can be taken rapidly and the average peak frequency corresponding to  $\omega_{12}$  is then readily attainable. With the value of the applied field  $B_0$ , it should again be possible to calculate the gyromagnetic ratio,  $\gamma$ .

However, there is a slight problem that hasn't been mentioned up to this point that renders the direct measurement of  $\gamma$  impossible. Due to electronic shielding, the magnetic field applied to the nucleus is not exactly  $B_0$ , and therefore, despite any level of accuracy in the measurement of  $\omega_{12}$ , its value corresponds to this unknown fraction of  $B_0$  that permeates to the nucleus. Although this electronic shielding seems very annoying if one wants an exact measurement of  $\gamma$ , we shall see in the next section why, at least as far as NMR as a spectroscopic technique is concerned, this can really be regarded as a huge advantage.

### **Chemical shift in practice**

The application of NMR to the identification of molecular constituents is made possible by the phenomenon known as the chemical shift. The chemical shift in an NMR spectrum arises from the inevitable shielding of the external magnetic field due to the electron cloud that surrounds the nucleus. Essentially, the orbital angular momentum of these electrons provides the electron cloud with a magnetic moment that opposes the applied magnetic field. This angular momentum in turn gives rise to its own minute magnetic field in this opposing direction.

In the context of a single atom, this shielding effect changes the amount of magnetic field that penetrates to the nucleus, obscuring the measurement of the gyromagnetic ratio. In practical terms, this is largely irrelevant because without molecular interactions, it remains constant and contributes nothing to the identification of the atom in question. On the other hand, when molecular interactions are present the shielding effect can be modulated to produce the chemical shift. In this way, the electron cloud surrounding a given atom's nucleus can be displaced to either increase or decrease the energy spacing for a given applied field compared to that found for the atom alone. For example, when a hydrogen bonds to a carbon, its electron is no longer as centrally localized about its nucleus, and the shielding is decreased. Furthermore, an oxygen is more electronegative than a carbon so when it bonds with a hydrogen, the hydrogen's shielding is decreased by an even larger amount. Therefore, the bonds of a given chemical species may be determined through NMR spectroscopy.

Still, the effects that arise from such changes in shielding are normally difficult to predict without complicated calculations. In practice, standard chemical shifts of various bond types are determined experimentally from known chemical samples, and unknown samples are compared to these characteristic baselines to determine structure. In a typical spectrum like the one below, the frequency (x axis of the plot) is aligned with a reference substance, which has been collectively agreed upon to contain zero chemical shift for a certain bond. The frequency values are then divided by the frequency of the reference bond to give the format in ppm—thereby removing the dependence upon magnetic field.

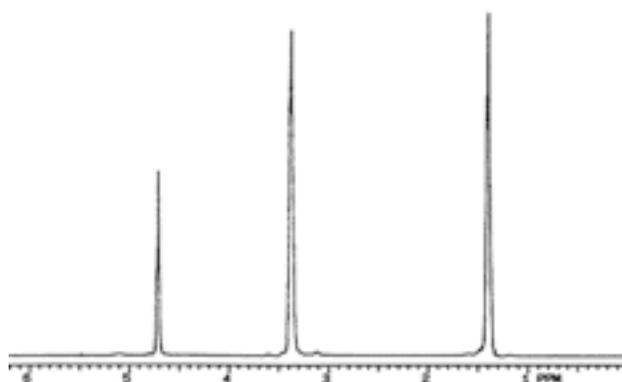


Figure 1. A typical NMR spectrum normalized for comparison with reference spectra

With a spectrum in hand, the peaks can be compared to previously recorded peak values such as those contained in Figure 2.

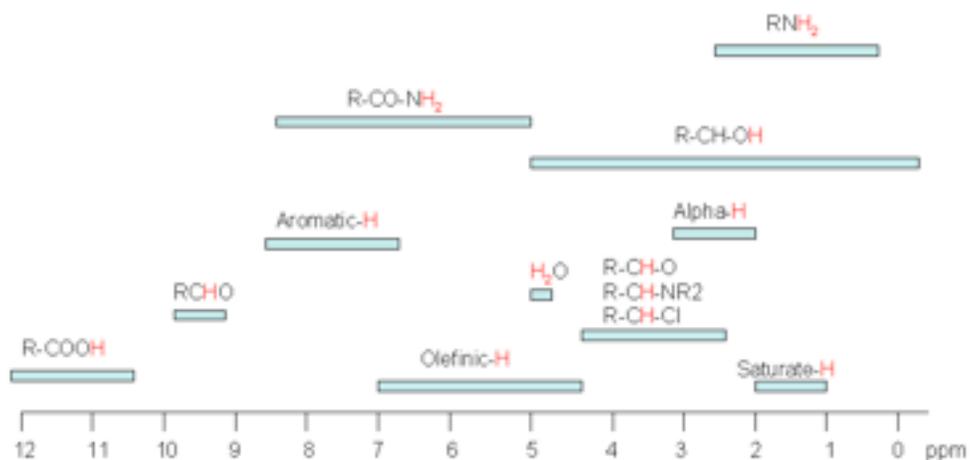


Figure 2. Common NMR spectrum peak locations for various bond types.

These heuristic methods are evidently not unique since the windows are wide, and there is commonly much overlap between different bonds. Nevertheless, this method has been applied to the study of chemistry many times, and much useful information has been garnered from it. Although NMR used in this way is extremely useful as is, it is very interesting and potentially very important to consider just how well one could calculate the chemical shift of a substance. Much work in quantum chemistry has centered around such techniques in the hope that NMR data might be made even more transparent and informative.

### Calculation of chemical shifts

The chemical shift arises entirely from the variation of the shielding of an atom subjected to different deformations of its electron environment due to their attraction to other nearby nuclei. Therefore, the problem lies in determining the correct magnetic field felt by the nucleus after accounting for this. To proceed, define the effective magnetic field felt by the nucleus as

$$B_{\text{eff}} = B_0(1-\sigma)$$

Now, the problem has been reduced to finding the factor  $\sigma$ .

The calculation of  $\sigma$  comes via several rounds of perturbation expansions of the energy of the field in question, but by the end of this the magnitude of  $\sigma$  can be determined through the following

$$E_{\sigma} = \langle \phi_0 | \mathbf{A}_k \cdot \mathbf{A}_0 | \phi_0 \rangle + \text{Re} \langle \phi_0 | 2\mathbf{A}_k \cdot \mathbf{p} + \mathbf{e} \cdot \mathbf{B}_k | \phi_{010} \rangle$$

where  $\mathbf{A}_k$  and  $\mathbf{B}_k$  are the magnetic field and potential arising from the  $k^{\text{th}}$  nucleus, and  $\mathbf{A}_0$  comes from the external field. The various  $\phi$  are different non-relativistic corrections to the electronic wave function in question and  $\mathbf{p}$  and  $\mathbf{e}$  are the nuclear and electronic spin moments. This energy tensor can be directly related to the shielding factor  $\sigma$  because this energy is in a roundabout way controlled by the electron density which is directly responsible for the modulation of the magnetic field. Although  $\sigma$  is technically a tensor, we regard the quantity as the average value over all directions since this is the only value that could possibly be measured with an ensemble of randomly oriented molecules in an NMR apparatus.

Taking these factors into account, Lamb (1941) and Ramsey (1953) calculated the first and second terms in the equation for  $E_{\sigma}$  and found equations for what are termed the diamagnetic ( $\sigma_d$ ) and paramagnetic ( $\sigma_p$ ) shielding.

$$\sigma_d = e^2/3mc^2 \Sigma \langle 1/r_i \rangle$$

$$\sigma_d = (\alpha^2 a_0^2 / 6\beta m M) (2Z\beta m / M a^3 - m B_N / M)$$

The  $\sigma_d$  equation includes the expectation value of the reciprocal of the distance from each electron to the nucleus. The  $\sigma_p$  equation includes many terms including the Bohr radius  $a_0$  the number of protons  $Z$  the fine structure constant  $\alpha$ , and the mass of the proton and the electron  $M$ ,  $m$ . Further details on these can be found in *Calculation of NMR and EPR Parameters*. These two calculations remain widely regarded as a nearly complete determination of the chemical shift for light elements. There is a relativistic theory of these magnetic properties, which is necessary for heavy elements, but the contributions of Lamb and Ramsey are still respected as some of the most influential of quantum chemistry. In addition, Ramsey developed a theory for the spin-spin or  $\mathbf{J}$  coupling of two nuclei—another important factor in determining structure from NMR spectra.

## Conclusions

Although NMR is frequently recounted in terms of a classical matter-radiation interaction or even perhaps as an analogy with a classical rotating body, the quantum mechanical formalism is sufficient to explain the observed phenomena. In addition, FT-NMR can be regarded as a time-dependent perturbation with three time domains ( $t < 0$ ,  $0 < t < t_f$ , and  $t_f < t$ ). Finally, despite the sufficiency of treating chemical shift empirically, a quantum chemical approach can be taken to derive the dependence of chemical shift on electronic environment, and with suitable computational techniques can be used to help predict structure from NMR spectra.

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