Lecture 5: One-dimensional NMR

In Lecture 4, we discussed the TLS problem in great detail dealing with a variety of coupling terms: real and constant, complex and constant, and oscillatory. The vast majority of problems in spectroscopy fall into one of these categories. In this lecture, we will discuss the physical origin of the coupling terms in nuclear magnetic resonance: Zeeman interaction, chemical shift, indirect interaction, and, finally, dipolar interactions. In lecture 6, we will discuss the radiation-matter interaction that is central to optical spectroscopy. In particular, we will introduce the definition of the polarization, dipole approximation, and formalism of nonlinear spectroscopy. Finally, we will discuss the system Hamiltonian in some detail for a variety of molecular systems.

5.1. Zeeman Interaction

We begin by considering what happens to a nuclear spin in a magnetic field. The atomic nucleus of an atom is composed of protons and neutrons (nucleons) tightly packed together. These particles, like electrons, undergo motion, and interact strongly with one another. Remarkably, despite the strong nuclear force, the nucleons do not crash into one another and destabilize the nucleus. The resolution of this problem comes from quantum mechanics; just like electrons, the nucleus has discrete energy levels, which properly compartmentalizes the particles and stabilizes them according to the same quantum mechanical rules as all other fermions. For instance, Pauli's exclusion principle guarantees that no two fermions can occupy the same state; therefore, nucleons occupy discrete energy levels, or if they occupy the same energy level they must do so with opposite spin. Owing to the strong nuclear force, the energy difference between nuclear levels is on the order of tens to hundreds of keV. We will see shortly that this implies the relevant states from the NMR perspective always reside in the ground nuclear state at all reasonable magnetic fields strengths. This fact facilities the use of the Wigner-Eckart theorem, which we will briefly discuss.

In constructing the Hamiltonian for this system, we begin with the classical energy of a magnetic moment, μ, in an external field, $\mathbf{H}$:

$$E = -\mu \cdot \mathbf{H}$$

How do we get from the magnetic moment to a quantum mechanical operator? First, we see that the magnetic moment is a vector, which can be transformed by rotations about x, y, and z. Now, recall the Pauli matrices that we introduced in lecture 2. These are operators, but they obey commutation relations essentially identical to those of infinitesimal rotation matrices,

$$[I_x, I_y] = iI_z$$

$$[I_y, I_z] = iI_x$$

$$[I_z, I_x] = iI_y$$

HW 1: Derive the commutation relations for rotation matrices, $R_{x,y,z}(\epsilon)$. Hint: since $\epsilon \ll 1$, Taylor expand up to second order. ♣

The point of all of this is that $\mathbf{I} \equiv [I_x, I_y, I_z]$ and μ transform in the same way. According to the Wigner-Eckart theorem, as long as we are in the ground nuclear state (so that coupling between different nuclear states can be ignored), then these two 'vectors' are identical up to a proportionality constant. This constant is dependent on the specific nuclear structure of the atom and is very difficult to calculate, although relatively straightforward to measure; it is called they gyromagnetic ratio and it depends on the many factors including the atomic mass **Note:** Classically, the gyromagnetic ratio is simply given by $q/2m$, where q is the charge and m is the mass. ♦ The classical magnetic moment and the spin angular momentum operators are then related: $\boldsymbol{\mu} = \gamma \mathbf{I}$, where γ is the gyromagnetic ratio. Now, we are in a position to state the Zeeman interaction quantum-mechanically:

$$H_Z = \gamma \mathbf{I} \cdot \mathbf{H}$$

When the field is oriented along one particular direction, say z, then we have

$$H_Z = \omega_I I_z$$

where $\omega_I = \gamma B_z$ is called the Larmor frequency. **Note:** **B** and **H** are not exactly the same, but for our purposes we will ignore the difference. Technically, **B** is the external field, but **H** includes contributions from the induced field (most materials possess a magnetic susceptibility that effects the external field). ♦

HW 2: At a field of 7T, what is the Larmor frequency for ^{1}H and ^{13}C? What magnetic field is a 900 MHz NMR? Hint: You can look up tables of γ online. The advertised NMR frequency corresponds to protons (can you think why?) ♣

HW 3: At the same field, show that our assumption about being in the ground nuclear state is indeed valid. Hint: The energy splitting between nuclear states is ~100 keV. You can think about this problem in terms of perturbation theory or more directly in terms of our analysis of the TLS. ♣

Next, let us carefully analyze what happens to a single nuclear spin when it is placed in a magnetic field. Prior to the field, the magnetic moment is randomly oriented. The system is in a state $|\Psi\rangle$ that is superposition of the eigenstates of the Zeeman Hamiltonian. Therefore, the field induces dynamics immediately after it is applied. **Note:** A little later we will discuss what happens at thermal equilibrium. ♦ The time-evolution of the state of the system is described by the Schrodinger equation (for states) or by the Liouville equation (for density operators). We have to ask the question of what is $\langle \mathbf{I} \rangle (t)$. This is easily computed to give

$$\langle I_x \rangle (t) = \langle I_x \rangle (0) \cos(\omega_I t) - \langle I_y \rangle (0) \sin(\omega_I t)$$

$$\langle I_y \rangle (t) = \langle I_x \rangle (0) \sin(\omega_I t) + \langle I_y \rangle (0) \cos(\omega_I t)$$

$$\langle I_z \rangle (t) = \langle I_z \rangle (0)$$

HW 7: Verify this result using the density matrix. Write equations for the transverse components in matrix form and comment on the physical interpretation of these results. ♣ From this result, we see that the expectation value of the transverse spin operators at time *t* is a rotation of the transverse spin operators at time 0 about the *z*-axis with frequency ω_I. To summarize, in the absence of a magnetic field, the magnetic moment associated with each individual spin is randomly oriented. Application of the field causes the spin to precess about the *z*-axis forming a cone with a conical angle dependent on the initial direction of the magnetic moment.

5.2. Chemical-Shift and Indirect Interaction Tensor

Thus far we have discussed nuclear spins. Of course, molecules also have electron spins, which are either paired or unpaired in the ground electronic state. When the total electron spin is 0, the molecule is diamagnetic, while when there is one or more unpaired electron it is paramagnetic. The latter is responsible for generating signals in electron paramagnetic resonance (EPR) spectroscopy. EPR is an extremely powerful technique, but it will not be a major focus of this course. **HW 8:** Approximately what frequencies can one expect EPR to operate at? Justify your answer. Hint: Remember the discussion of the gyromagnetic ratio. Assume a field of about 0.35 T. ♣ Nuclear magnetic resonance (NMR) spectroscopy deals almost exclusively with atoms from diamagnetic molecules. The electrons of these atoms possess spin as well as orbital angular momentum. In short, electrons move around the nucleus in well-defined orbitals and from classical mechanics (e.g. Maxwell's equations) we know that current density induces a magnetic field. In a diamagnetic molecule, this field sums to zero. However, in the presence of an external field, an additional electronic current is induced, which in turn induces an additional magnetic field. The local field is dependent on the orientation of the molecule relative to the external. ♠ Supplementary Notes ♠. Therefore, one needs a tensor rather than a scalar to describe the local field in three-dimensional space. The tensor is a 3x3 matrix with components $xx, xy, xz, yx, \ldots$ The Hamiltonian describing this effect can be written as

$$H_{CS} = \gamma \mathbf{I} \cdot \boldsymbol{\sigma} \cdot \mathbf{H}$$

where $\boldsymbol{\sigma}$ is the so-called chemical shift tensor. Because the molecule is isotropically rotating in a liquid, the tensor gets averaged to a single scalar value. Therefore, we have,

$$H_{CS}^{iso} = \gamma \sigma^{iso} \mathbf{I} \cdot \mathbf{H}$$

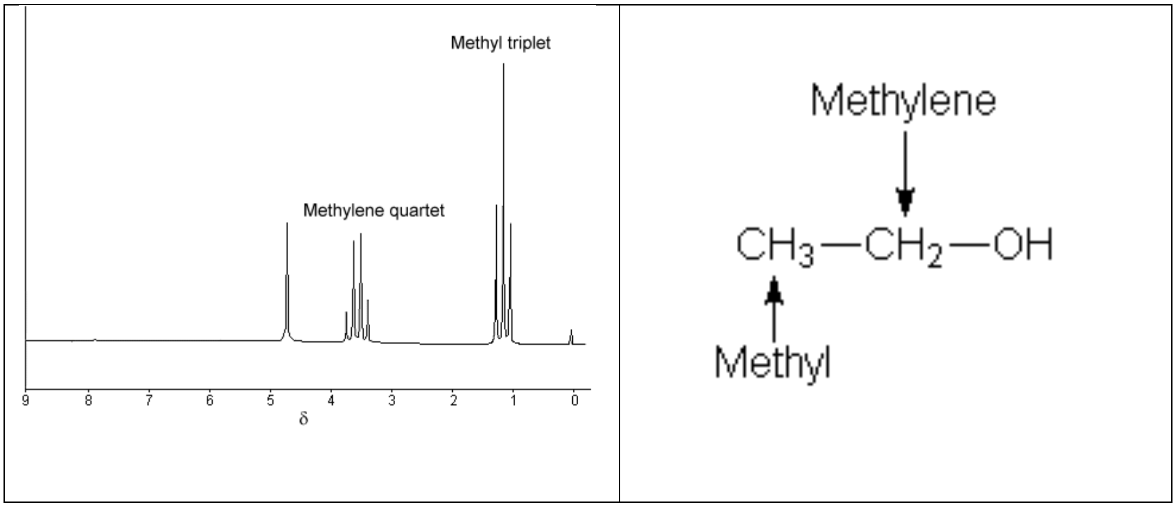
Later when we get into a discussion of statistics, we will see that $\sigma^{iso} = tr(\boldsymbol{\sigma})$. **Note:** We will drop the superscript 'iso' unless otherwise noted since our analysis of NMR is primarily in liquids. ♦ **HW 9:** Write the total Hamiltonian including the Zeeman and isotropic chemical-shift terms. What is the Larmor frequency? ♣

The chemical-shift interaction only describes the effect of the additional local field produced by the external field. Notice, it is just the Zeeman term discussed earlier but with the field, **H**, replaced by $\boldsymbol{\sigma} \cdot \mathbf{H}$. In other words, this effect is linear in the magnetic moment.

There is another effect, which arises from the magnetic interaction between the nuclear and electron spins combined with the exchange interaction between the electrons forming the bond between nuclei. This effect, known as the indirect coupling, or J-coupling, is dependent on the magnetic moments of bonded atoms and hence is bilinear with respect to the two operators. It has the form

$$H_{ind} = \mathbf{I}_1 \cdot \mathbf{J} \cdot \mathbf{I}_2$$

Let us try to understand the physics in a little more detail. Consider two nuclei connected by a sigma bond. The nucleus of one of the atoms interacts magnetically with the electron of the same atom. As it turns out, the spin of the electron is more favorably aligned with the antiparallel orientation of the nuclear spin. This seems counterintuitive since magnetic moments are more favorably aligned parallel to one another. However, the electron spin is oppositely oriented with respect to its electron magnetic moment, in contrast to the nuclear spin which is aligned with its nuclear magnetic moment. Now consider what happens at the other bonded atom. We know that due to electron exchange, the electron spins in the sigma bond must be antiparallel to one another. The nuclear spin on the other atom also favors an antiparallel orientation with respect to the electron on the same atom. Therefore, the nuclear spins on the two bonded atoms prefer a parallel orientation with respect to one another. In other words, there is a difference in energy between parallel orientation and antiparallel orientation between the two nuclear spins – hence, the origin of the indirect interaction. As you can imagine, this energy difference is very small. Remarkably, it does not depend on the external magnetic field; therefore, J-coupling between nuclei can be observed even at zero field!!! The reason that **J** is a tensor is that it depends on the details of the atomic orbitals, which have a three-dimensional representation. For any of you that have ever taken an NMR spectrum, there is another important observable related to the indirect interaction, namely the multiplet spectra. Let us try and understand the physics behind this effect. Consider ethanol, CH3-CH2-OH. The methylene peaks are split into a quarter, while the methyl peaks are split into a triplet. If we consider the methylene protons for instance, we see that there are two possible spin states of the two equivalent nuclear spins, $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$. Each spin state produces a local field at the site of the methyl protons. The fields produced by the parallel configurations are equal in magnitude, but opposite in signs, while the the antiparallel configurations produce no net field at the site of the methylene protons. Therefore, we see that the methyl protons will produce three peaks, with a ratio of 1:2:1. **HW 10:** Use similar reasoning to justify the methylene quarter. ♣. **HW 11:** Rationalize the ordering of the chemical shifts for the methyl, methylene, and hydroxyl protons. ♣ **HW 12**: Prove the $n+1$ rule based on these arguments, i.e. the multiplicity of a multiplet is given by the number of protons in neighboring atoms, *n*, plus one. ♣



5.3 RF Field

Next, we will analyze what happens to the spins upon application of an RF field. We will also discuss measurement of the NMR signal. Fortunately, the first part of the problem was almost entirely dealt with in Lecture 2. Let us briefly review. As usual, we start with the Hamiltonian:

$$H = \omega_I I_z + V(t)$$

where $V(t)$ represent the RF field. Now, before giving away the operator form of the field, lets think for a minute on what are some good candidates. First, we know that any operator in this

Hilbert space must belong to the basis spanned by $I_x, I_y, I_z, \mathbb{1}$. Remember, the point of the RF field is to somehow observe the Larmor frequency or indirect interactions (not shown for sake of brevity), which provides the information we want (e.g. NMR spectrum). If we apply an operator $\propto I_z$ then we will essentially do nothing! **HW 13:** Why is this the case? ♣ Therefore, we have to use operators I_x and I_y, so-called transverse spin operators, in order to induce dynamics that we may subsequently observe. From our discussion of Rabi oscillations in Lecture 2, we already know the answer: $V(t) = 2\omega_{RF}\cos(\omega_0 t)I_x$ (the factor of 2 will become apparent in a moment). This operator, will cause transitions from the two spin states, $|\pm\rangle$, and show up as absorption of radiation. At this point, one has two options

1. Scan ω_0 and observe the change in amplitude of the absorbed radiation (in this case, a change in the current of the pickup coil). This is known as the continuous-wave (CW) method.
2. Apply a pulsed excitation and observe the free-induction decay (FID). This is known as pulsed NMR.

Either way, we have to understand the nature of the measurement before we analyze these two situations. We know that application of the field near resonance $\omega_0 \approx \omega_I$ will produce a superposition state between the two spin states. Let us make this statement more precise. The effective Hamiltonian for this RF field is given by

$$H_{eff} = (\omega_I - \omega_0)I_z + \omega_{RF}I_x$$

HW 14: Verify this. Also explain why it was convenient to place the factor of 2 in the RF interaction term used above. Hint: Go back to lecture 2 notes and change notation. ♣ Remember, this field is in the interaction representation, $A(t) = e^{-i\omega_0 I_z t}$. So we have, $\widetilde{\rho}(t) \equiv A(t)\rho(t)A^{\dagger}(t)$. **Note:** We will come back to the consequences of this 'rotating frame' a bit later. ♦ Therefore, the time evolution operator is given by $U(t) = e^{-iH_{eff}t}$. At equilibrium the density matrix is given by the partition function,

$$\rho(0) = \frac{e^{-H/kT}}{tr(e^{-H/kT})}$$

HW 15: Justify this argument. Hint: Think about the Boltzmann distribution and the definition of the density matrix. Remember to normalize. ♣ In the high temperature limit, $kT \gg \Omega_i$, so that we can approximate

$$\widetilde{\rho}(0) = \rho(0) \approx \mathbb{1} - \beta H_0$$

where $\beta \equiv (kT)^{-1}$ and $H_0 = \omega_I I_z$. HW 16: Prove this. ♣ Therefore,

$$\widetilde{\rho}(t) = U(t)\widetilde{\rho}(0)U^{\dagger}(t) = e^{-iH_{eff}t}\left(\mathbf{1} - \omega_I \beta I_z\right)e^{iH_{eff}t}$$

which gives, in the case of on-resonance excitation ($\omega_0 = \omega_I$),

$$\widetilde{\rho}(t) = \mathbf{1} - \frac{\omega_I}{kT} e^{-i\omega_{RF} I_x t} I_z e^{i\omega_{RF} I_x t}$$

We can ignore the identity operator as will become clear in a moment to finally give:

$$\widetilde{\rho}(t) = -\frac{\omega_I}{kT}\left(\cos(\omega_{RF}t)I_z + \sin(\omega_{RF}t)I_y\right)$$

This means that in the space defined by I_x, I_y, I_z, the effect of the RF field is to rotate the spin about the *x*-axis into the *y*-*z* plane, by an angle, $\theta = \omega_{RF}t$. This process is called a nutation in the NMR terminology, but it is essentially a Rabi oscillation between spin states. **HW 16:** Verify the expression given above for the density matrix at time *t*. ♣ **HW 17:** Explain what is happening physically when the RF pulse is on. Hint: Remember that we are in the rotating frame! ♣ Of course, the RF pulse cannot be resonant with all the frequencies in the molecule (or more precisely, the carrier frequency, ω_0, cannot be resonant with all the frequencies in a molecule with inequivalent spins). Therefore, we need to analyze what happens off-resonance, $\omega_0 \neq \omega_I$. If we examine the form of H_{eff}, we see that it can be represented by a vector with I_x component ω_{RF} and I_y component $\Delta \equiv \omega_I - \omega_0$. Therefore, the effect of the time evolution operator on I_z is to rotate the spin about this effective axis by an angle $\theta = \sqrt{\Delta^2 + \omega_{RF}^2}$. **HW 1*:** Prove this mathematically. (this is a bit of a pain) ♣ **HW 18:** At what time, t_{90}, is $\theta = \pi/2$? In what spin operator is the density matrix at this time? Notice, this is the same result as the Rabi formula; that is, while the RF pulse is on, the system oscillates between I_z and $-I_z$ at a frequency θ. Actually, this isn't technically correct because the spin state is initially I_z, so that only the spins that are on resonance can reach $-I_z$. Spin that are off-resonance can never reach $-I_z$ exactly. **HW 19:** Using geometric arguments, what is the "closest" the system can reach to $-I_z$? In other words, what is the maximum that the spin can nutate (i.e. rotate by means of the RF pulse) towards $-I_z$? ♣ For the moment, we will consider the case when $\omega_{RF} \gg \Delta$, so that we can ignore off-resonance effects (we will have more to say about this a bit later). Lets think what happens when we turn the pulse off. The system is in a certain spin state completely determined by θ and t_θ, the duration of the RF pulse. Now the system is subject to free-evolution according to the system Hamiltonian, which itself is dominated by the Zeeman interaction. Therefore, the spin begins to rotate around the *z*-axis. It therefore, makes no sense to detect the spin along *z*, since $\langle I_z \rangle(t) = \langle I_z \rangle(0)$. **Note:** The NMR signal is proportional to the *change* in magnetic field; the *principle of reciprocity* states that $\xi = -\left(\frac{\partial}{\partial t}\right)(\mathbf{B}_1 \cdot \mathbf{m})$, where $\mathbf{B}_1$ is the magnetic field and $\mathbf{m}$ is the magnetic dipole. This comes directly from Maxwell's equation in which the induced emf is given by the change in the classical interaction energy between a magnetic field and a magnetic dipole. We have not talked about the idea of bulk magnetization yet, which is critical to understand the NMR signal in the bulk, but we will soon. ♦ This leaves us with the option of detecting the spin along the transverse direction. This can be done by an operator, $I_+ \equiv I_x + iI_y$, the so-called angular momentum raising operator (we will discuss physically how this is done a bit later). In order to maximize $\langle I_+ \rangle$, we need to choose t_θ such that spin state lies in the transverse plane. This is accomplished when $\omega_{RF} t_\theta = 90^o$. Intuitively, this should make sense because rotating I_z by 90^o about I_x gives I_y. Lets prove this mathematically using the density matrix:

$$e^{-i\omega_{RF} I_x t_\theta} I_z e^{i\omega_{RF} I_x t_\theta} = I_x \cos(\omega_{RF} t_\theta) + I_y \sin(\omega_{RF} t_\theta) = I_y$$

The system now undergoes free-evolution (note that we are no longer in the rotating frame):

$$\rho(t) = \beta\omega_I e^{-iH_0 t} I_y e^{iH_0 t} = \beta\omega_I e^{-i\omega_I I_z t} I_y e^{i\omega_I I_z t}$$

We have ignored indirect interactions for now, but have included the chemical shift, $\omega_I = \gamma B_z - \sigma^{iso}$. Next, lets calculate the signal

$$\langle I_+ \rangle(t) = tr\left(I_+ \rho(t)\right)$$

Note, that we used the fact that $tr\left(I_+(t)\rho(0)\right) = tr\left(I_+\rho(t)\right)$. **HW 20:** Prove this. Comment on what this means physically. ♣ In order to calculate this we need a couple of useful identities for spin-1/2:

$$tr\left(I_+ I_x\right) = tr\left(I_x^2\right) = \tfrac{1}{2}$$

$$tr\left(I_+ I_y\right) = itr\left(I_x^2\right) = \tfrac{i}{2}$$

$$tr(I_x I_y) = 0$$

The last identity is not explicitly used here, but is useful for many other calculations that we'll do soon. **HW 2***: Derive the identities for any spin-I. ♣ Finally, we have

$$\langle I_+ \rangle(t) = \beta\omega_I e^{i\omega_I t}$$

We can see that the amplitude of the signal is given by $\beta\omega_I$ and that it oscillates at the Larmor frequency. **HW 21:** Calculate the amplitude of the signal for protons at a magnetic field of 7 T at room temperature. ♣ Upon Fourier transformation we get

$$S(\omega) \propto \mathscr{F}\left(\langle I_+ \rangle(t)\right) = \beta\omega_I \delta(\omega - \omega_I)$$

which is the pulsed NMR (or Fourier Transform NMR) spectrum! ♠ In the supplementary material, we will discuss the benefits of FT NMR over the CW method (in which, Richard Ernst won the Nobel Prize for advancing!) ♠.

Additional Problems:

HW 22: Analyze the pulsed NMR experiment for the case of on-resonance, but include explicitly the indirect coupling term in the weak-field limit, $H_J = JI_zS_z$. Plot the NMR spectrum using Matlab or Mathematica (or whatever other program you desire).

HW 23: In this problem we will examine the spin echo effect. Later, we will discuss the photon echo effect which is conceptually related.

HW 24: In this problem, we are going to examine why equivalent spins do not give rise to splitting among themselves. That is, the protons of say the methylene group do interact with one another, yet there is no observable NMR signature from these interactions. I will guide you through the analysis and let you fill in the missing steps.

First, we have to recognize that in liquids, the molecules rotate much faster than the NMR time scale. **A.** What is the typical rotational correlation time for a small molecule such as ethanol? What defines the NMR time scale in this context? ♠ Therefore, the indirect interaction can be written as $H_{ind} = J\mathbf{I}_1 \cdot \mathbf{I}_2$, where *J* is the isotropic average of the tensor **J**. We can write the Hamiltonian for a system consisting of two groups of equivalent spin I^k and S^n as

$H = H_1 + H_2$, where

$$H_1 = \omega_I \sum_k I_z^k + \omega_S \sum_n S_z^n + J \sum_{n,k} \mathbf{I}^k \cdot \mathbf{S}^n$$

$$H_2 = \sum_{k,l} J_{kl} \mathbf{I}_k \cdot \mathbf{I}_l + \sum_{n,m} J_{nm} \mathbf{S}_n \cdot \mathbf{S}_m$$

H_1 represents the Larmor frequencies (and chemical shifts) and isotropically averaged indirect-interaction. H_2 represents the indirect interactions between equivalent spins. B. Show that $[H_1, H_2] = 0$, i.e. the two Hamiltonian terms commute. ♠ With regards to the measurement, we will either detect spin I or spin S. Obviously, it doesn't matter since the problem is symmetric. If we detect spin I, we need to evaluate

$$\langle \textstyle\sum_i I_+^i \rangle(t) = tr\left\{U(t) \textstyle\sum_i I_+^i U^\dagger(t)\rho(0)\right\}$$

where $U(t) = e^{i(H_1+H_2)t}$. Since $[H_1, H_2] = 0$, we have $U(t) = e^{iH_1t}e^{iH_2t}$ (see auxillory notes). Furthermore, we have $[\sum_i I_+^i, H_2] = 0$. Therefore,

$$\langle \textstyle\sum_i I_+^i \rangle(t) = tr\left\{e^{iH_1t} \textstyle\sum_i I_+^i e^{-iH_2t}(t)\rho(0)\right\}$$

C. Verify this result. ♠ Therefore, H_2 doesn't actually affect the signal and we can effectively ignore it. There is a very important idea buried in the math. Terms in Hamiltonian that commute with the observable and with other terms in the Hamiltonian do not affect the dynamics. It is often times advantageous to split the Hamiltonian into commuting terms because it allows flexibility in the time-evolution operator because one can use the convenient relation, $e^{A+B} = e^A e^B$. To reiterate, if either *A* or *B* commute with the observable then they cannot have an effect on the measurement!