Chapter 4 QUANTUM MECHANICAL DESCRIPTION OF NMR

Schrodinger Equation: $$i\hbar\frac{d\Psi}{dt} = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V_o\Psi = \mathcal{H}\Psi$$

In the above equation, H, or the Hamiltonian, can also be described as an operator. Operators are mathematical representations of observables, such as energy, that are applied to wavefunctions. The Hamiltonian is a very important operator. Not only can it provide the energy associated with a state of the system, but it also determines how the system evolves in time.

The application of an operator onto a wavefunction returns the values of the observable and another wavefunction. If the same wavefunction is returned, then these wavefunctions are given a special name, eigenfunctions1, and the observable is called an eigenvalue. For example, the application of the Hamiltonian to one of its eigenfunctions will return the same eigenfunction multiplied by the energy of that state: $\mathcal{H}\Psi = E_\Psi\Psi$

Here, Ψ is an eigenfunction of H, and is associated with an eigenvalue of EΨ. Wavefunctions that are eigenfunctions of the total energy are referred to as *stationary states* because only their phase changes during time evolution:

$i\hbar\frac{d\Psi}{dt} = E_\Psi\Psi$ and the solution of this equation is: $\Psi(t) = \Psi(0)e^{-i\frac{E_\Psi}{\hbar}t}$

The quantum mechanical description of NMR will utilize wavefunctions to represent the current state of the magnetization at any point in an experiment. The Hamiltonian that is present at that time will describe how the magnetization (wavefunction) will change with time. Therefore our goal is to describe the wavefunction associated with the initial state of the NMR experiment, and then use the Hamiltonian to determine the evolution of the magnetization as the experiment progresses, up to and including, the detection of the final signal.

4.1.1 Vector Spaces and Properties of Wavefunctions

Any arbitrary state of the system can be described as: $\Psi = \sum_{i=1}^{n} c_i u_i$

Where u_is are the basis vectors which are orthogonal to each other, i.e. $\delta_{mn} = \int_{-\infty}^{+\infty} u_m^* u_n d\chi$

c_i is the projection of the state of the system onto the ith basis vector.

The probability, P_m, that any given system can be found in any particular basis state m is given by: $P_m = c_m^* c_m$

4.2 Expectation Values

The average, or measured, value of any observable can be extracted from the wavefunction of the system by calculating the expectation value. For example, the expectation, or observed, value of the energy of a system $< E >= \int \Psi^* \mathcal{H} \Psi d\chi$

and that for the x-component of the spin angular momentum: $< I_x >= \int \Psi^* I_x \Psi d\chi$

If the system is described as a mixture of the basis states $\Psi = \sum c_k u_k,$ then the expectation value is the weighted average, using the energy of the system as an example:

$$< E > \; = \; \int \Psi^* \mathcal{H} \Psi d\chi \; = \; \sum_k P_k E_k$$

For a system in a pure state k then <E> = E_k since P_k = 1.

4.3 Dirac Notation

In the case of NMR, the wavefunctions will represent different states of the nuclear spin. Since there are no spatial coordinates associated with these wavefunctions it is necessary to develop a different representation of wavefunctions, their basis vectors, operators, and associated expectation values. This representation was developed by Dirac and is often referred to as the 'Bra-Ket' notation.

4.3.1 Wavefunctions in Dirac Notation

The individual basis functions, u_m, are represented as $|u_m >$. The complex conjugate of the basis functions are written as $< u_m|$. The orthonormality relationship is written as:

$$\delta_{nm} =< u_n|u_m >= \int u_n^* u_m d\chi$$

Any arbitrary wave function is represented as: $\Psi = \sum_{i=1}^{n} c_i|u_i >$

The individual coefficients, c_m are obtained in the usual way: $c_m = \int u_m^* \Psi d\chi =< u_m|\Psi >$

In systems with a finite number of eigenstates it is convenient to represent wavefunctions as vectors. In this representation, the basis vectors the wavefunction of an arbitrary system can be written as a vector composed of the coefficients of its eigenstates:

$$\Psi = \begin{bmatrix} < u_1|\Psi > \\ < u_2|\Psi > \\ < u_3|\Psi > \\ < u_4|\Psi > \\ \vdots \\ < u_n|\Psi > \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ \vdots \\ c_n \end{bmatrix}$$

4.3.3 Operators in Dirac Notation

The Bra-Ket representation can be extended to operators. In this case, operators are represented by a matrix, whose elements are defined as: $A_{ij} =< u_i|A|u_j >$

For example, the Hamiltonian operator for a particle in a box is:

$$\mathcal{H} = \begin{bmatrix} E_1 & 0 & 0 & . \\ 0 & E_2 & 0 & . \\ 0 & 0 & E_3 & . \\ . & . & . & . \end{bmatrix}$$

4.3.4 Expectation Values in Dirac Notation

Using the example of the energy of the system, the expectation value of an operator is given as:

$$< E > = \int \Psi^* \mathcal{H} \Psi d\chi = [c_1^* \ c_2^* \ c_3^* \ldots] \begin{bmatrix} A_{11} & A_{12} & A_{13} & \ldots \\ A_{21} & A_{22} & A_{23} & \ldots \\ A_{31} & A_{32} & A_{33} & \ldots \\ \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{bmatrix}$$

4.4 Hermitian Operators

Hermitian operators are those operators whose eigenvalues are real. Since the eigenvalues are real, the expectation values are also real. Therefore Hermitian operators correspond to physically observable properties of the system.

4.4.1 Determining Eigenvalues

Until this point we have assumed that the basis vectors are eigenvectors of the Hamiltonian. As such, $Hu_k = E_k u_k$. This assumption implies that the matrix form of H is diagonal. This form of the Hamiltonian is convenient in that the energies of the different basis states can be read from the diagonal elements. This simple diagonal form of the Hamiltonian exists only in one particular coordinate frame. In this frame the eigenfunctions of the Hamiltonian also have a simple form, e.g. $u^{\dagger}_3 = [0\ 0\ 1\ 0\ldots]$ and the eigenvalues form the diagonal elements of the operator. For example, consider the following example of a Hamiltonian and associated wave functions for a spin 1/2 system:

$$\mathcal{H} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \qquad u_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \qquad u_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

The eigenvalues (λ_n) are immediately seen to be: $\lambda_1 = 1$, $\lambda_2 = -1$.

Often it is necessary to work in a different reference frame to describe the state of the system. In this case, the basis vectors will no longer have a simple form and the matrix representation of the Hamiltonian will be non-diagonal. For example, if the coordinate frame is rotated by 45°, the above Hamiltonian appears as follows ……..

4.5.2 Time Evolution of Observables

4.5.3 Trace of an Operator

$$Trace[A] = \sum_{1}^{n} < u_i|A|u_i >$$

4.5.4 Exponential Operator

The operator, e^A, is defined as:

$$e^A = \sum_{n=0}^{\infty} \frac{A^n}{n!}$$

If A is Hermitian, then e^A is also Hermitian. Furthermore, if the eigenvalue of A is λ, then the eigenvalue of e^A is e^{λ}. If two operators, A and B, commute then the following is true:

$$e^A e^B = e^B e^A = e^{A+B}$$

4.5.5 Unitary Operators

An operator is unitary if its inverse and its adjoint are equal:

$$U^{\dagger}U = UU^{\dagger} = UU^{-1} = 1$$

Unitary operators do not affect the lengths of vectors, just their direction. Therefore unitary operators perform rotations on wavefunctions and other operators. Consider the application of a Unitary operator on two wavefunctions:

$$|\Psi 1> = U|\Phi 1>; \qquad |\Psi 2> = U|\Phi 2>$$

The scalar product of these two functions is invariant to the unitary transformation:

$$< \Psi 1|\Psi 2> = < \Phi 1|U^{\dagger}U|\Phi 2> = < \Phi 1|\Phi 2>$$

4.5.6 Exponential Hermitian Operators

If an operator *A* is Hermitian, then the operator W, defined as, $W = e^{iA}$ is unitary.

4.6 Hamiltonian and Angular Momentum Operators for a Spin-1/2 Particle:

Stern-Gerlach experiment demonstrating the presence of quantized spins. For the spin $\frac{1}{2}$ system there can be only two states, $+\hbar/2 \text{ and } -\hbar/2$.

In Dirac's notation the wave functions of these two states can be written as :

$$u_{+1/2} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad u_{-1/2} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

These are orthonormal.

$$< u_{+1/2}|u_{+1/2} >= \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = 1 \qquad < u_{+1/2}|u_{-1/2} >= \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = 0$$

Using these wavefunctions, the matrix form of the operator, S_z, *is:*

$$S_z = \begin{bmatrix} < u_{+1/2}|S_z|u_{+1/2} > & < u_{+1/2}|S_z|u_{-1/2} > \\ < u_{-1/2}|S_z|u_{+1/2} > & < u_{-1/2}|S_z|u_{-1/2} > \end{bmatrix}$$

$$= \begin{bmatrix} < u_{+1/2}| + \hbar/2|u_{+1/2} > & < u_{+1/2}| - \hbar/2|u_{-1/2} > \\ < u_{-1/2}| + \hbar/2|u_{+1/2} > & < u_{-1/2}| - \hbar/2|u_{-1/2} > \end{bmatrix}$$

$$= \begin{bmatrix} +\hbar/2 < u_{+1/2}|u_{+1/2} > & -\hbar/2 < u_{+1/2}|u_{-1/2} > \\ +\hbar/2 < u_{-1/2}|u_{+1/2} > & -\hbar/2 < u_{-1/2}|u_{-1/2} > \end{bmatrix} = \begin{bmatrix} +\hbar/2 \cdot 1 & -\hbar/2 \cdot 0 \\ +\hbar/2 \cdot 0 & -\hbar/2 \cdot 1 \end{bmatrix} = +\frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

The other two operators for angular momentum are obtained by the use of the raising and lowering operators, which are defined as follows:

$J_+ = J_x + iJ_y$; $J- = J_x - iJ_y$

S_x and S_y can be obtained from a linear combination of the raising and lowering operators: $S_x = 1/2[J_+ + J_-]$; $S_y = 1/2i[J_+ - J_-]$

The raising operator increases the z-component of the angular momentum by one unit and is defined by the following equation:

$$J_+|j,m>=\hbar\sqrt{j(j+1)-m(m+1)}|j,m+1>$$

$$J_-|j,m>=\hbar\sqrt{j(j+1)-m(m-1)}|j,m-1>$$

In these equations, |j,m > represents a wavefunction with j as the quantum number for the total spin angular momentum and m is the quantum number of the z-component of the spin angular momentum. For a spin-1/2 system (j = m = 1/2) these simplify to:

$$J_+|u_{-1/2}>=\hbar|u_{+1/2}> \qquad J_-|u_{+1/2}>=\hbar|u_{-1/2}>$$

The raising operator cannot increase *m_z higher than +1/2 so, $J+|u_{+1/2}>$ gives a null* vector, represented by *Ø. Similarly, since the lowest value of m_z is -1/2, $J-|u_{-1/2}>$* also gives a null vector. The matrix representation of the raising and lowering operators are obtained in the same fashion as *S_z:*

$$J_+ = \begin{bmatrix} < u_{+1/2}|J_+|u_{+1/2} > & < u_{+1/2}|J_+|u_{-1/2} > \\ < u_{-1/2}|J_+|u_{+1/2} > & < u_{-1/2}|J_+|u_{-1/2} > \end{bmatrix} = \hbar\begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}$$

$$J_- = \begin{bmatrix} < u_{+1/2}|J_-|u_{+1/2} > & < u_{+1/2}|J_-|u_{-1/2} > \\ < u_{-1/2}|J_-|u_{+1/2} > & < u_{-1/2}|J_-|u_{-1/2} > \end{bmatrix} = \hbar\begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}$$

$$S_y = \frac{1}{2i}[J_+ - J_-] = \frac{\hbar}{2i}\left[\begin{bmatrix}0 & 1\\ 0 & 0\end{bmatrix} - \begin{bmatrix}0 & 0\\ 1 & 0\end{bmatrix}\right] = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}$$

Similarly:

$$S_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$$

In summary, the matrix representations for the three Cartesian components of angular momentum are:

$$S_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix} \quad S_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix} \quad S_z = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$$

The matrix representation of the Hamiltonian operator is proportional to Sz:

$$\mathcal{H} = -\frac{\hbar\omega_s}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} = -\omega_s S_z$$

Note that S_z and H are diagonal using these basis vectors. Therefore the basis vectors $u_{+1/2}$ and $u_{-1/2}$ are eigenvectors of both of these operators. The eigenvalues are simply the diagonal elements of the matrix form of the operator, for example:

$$S_z|u_{+1/2}> = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\begin{bmatrix}1\\ 0\end{bmatrix} = +\frac{\hbar}{2}\begin{bmatrix}1\\ 0\end{bmatrix} = \frac{\hbar}{2}|u_{+1/2}>$$

Since the operators Sz and H clearly share the same eigenvectors they must also commute with each other. Consequently the expectation value of Sz is time invariant under the influence of this Hamiltonian. In contrast, these basis vectors are not eigenvectors of the operators for transverse magnetization, S_x and S_y, as can be seen from the following:

$$S_x|u_{+1/2}> = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\begin{bmatrix}1\\ 0\end{bmatrix} = +\frac{\hbar}{2}\begin{bmatrix}0\\ 1\end{bmatrix} = \frac{\hbar}{2}|u_{-1/2}>$$

4.7 Rotations

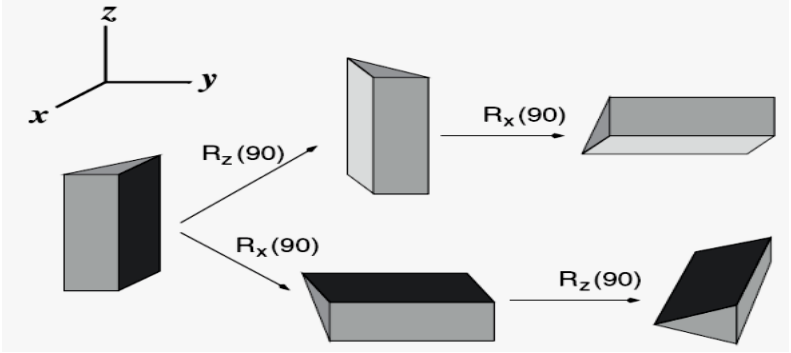
All NMR RF-pulse sequences (experiments) can be described as a series of rotations (i.e. pulses) applied to the system followed by time evolution of the system under the influence of various Hamiltonians. For example, the simple one pulse experiment involves a rotation of the magnetization by a 90◦ pulse followed by rotation of the transverse magnetization about the z-axis due to evolution of the system under the Hamiltonian, H. Therefore, it is important to develop operators that describe rotations. In doing so, we are developing a method of representing pulses as well as the free precession of spins in an NMR experiment.

4.7.1 Rotation Groups

rotation can be characterized by an axis of rotation and an amount of rotation. For example, the operator that describes a rotation of a degrees about the z-ax*is can* be written as: $R_z(\alpha) = \alpha\hat{k}$

In general $R_a(\alpha)R_b(\beta) \neq R_b(\beta)R_a(\alpha)$. However, two rotations performed along the same axis always commute.

$R_z(90)R_x(90)$ versus $R_x(90)R_z(90)$



4.7.2 Rotation Operators

Rotation operators change the orientation of wavefunctions and operators with respect to a fixed coordinate system. This should not be confused with the rotating frame of reference. Here, the wavefunctions rotate, not the coordinate frame.

The rotation operator for a rotation about u becomes: $R_u(\alpha) = e^{-i\sigma_u \frac{\alpha}{2}}$

In Dirac notation, the rotation operator is: $R_u(\alpha) = \begin{bmatrix} cos\frac{\alpha}{2} - i\, cos\theta sin\frac{\alpha}{2} & -i\, sin\theta sin\frac{\alpha}{2} e^{-i\phi} \\ -i\, sin\theta sin\frac{\alpha}{2} e^{i\phi} & cos\frac{\alpha}{2} + i\, cos\theta sin\frac{\alpha}{2} \end{bmatrix}$

4.7.2.1 Rotation Operator is Unitary

Rotations, by their very nature, do not affect any lengths or physical properties of the system, they simply rotate the system to a new orientation. Therefore, we expect the rotation operator to be unitary, $R^\dagger R = RR^\dagger = 1$. This can be easily seen by taking the product of R_u and $R^\dagger_u$.

$$R_u^\dagger(\alpha) = \begin{bmatrix} cos\frac{\alpha}{2} + i\, cos\theta sin\frac{\alpha}{2} & +i\, sin\theta sin\frac{\alpha}{2} e^{-i\phi} \\ +i\, sin\theta sin\frac{\alpha}{2} e^{i\phi} & cos\frac{\alpha}{2} - i\, cos\theta sin\frac{\alpha}{2} \end{bmatrix} \quad \text{Thus,} \quad R_u R_u^\dagger = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

4.7.3 Rotations of Wave Functions and Operators

Assume that our system can be described using a set of basis vectors, $|u_n\rangle$, with eigenvalues for an operator , A, of a_n: $A|u_n\rangle = a_n|u_n\rangle$

If we perform a rotation on the system, a new basis set is generated in the same coordinate system: $|u_n'\rangle = R|u_n\rangle$

These new basis vectors will be eigenvalues of the operator in the new form of the wavefunction: $A'|u_n'\rangle = a_n|u_n'\rangle$

The effect of rotations on operators: $A' = RAR^\dagger$

4.7.3.2 Example: Rotations about the x-axis

Rotations about the x-axis are equivalent to RF-pulses applied along the x-axis. In this case, the axis of rotation is specified as: θ = 90°, φ = 0°, giving the following rotation matrix: $R_x(\alpha) = \begin{bmatrix} cos(\frac{\alpha}{2}) & -isin(\frac{\alpha}{2}) \\ -isin(\frac{\alpha}{2}) & cos(\frac{\alpha}{2}) \end{bmatrix}$. For 90° rotation: $R_x(\pi/2) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix}$

If this operator was applied to $u_{+1/2}$:

$$u'_{+1/2} = R_x(\pi/2)u_{+1/2} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$$

This rotation has converted the original wavefunction, $u_{+1/2}$ to a linear combination of $u_{+1/2}$ and $u_{-1/2}$, indicating that a transition in the system has occurred due to the rotation, as would be expected for a 90° pulse.

The effect of the 90° rotation on the Hamiltonian operator is:

$$\mathcal{H}' = R\mathcal{H}R^{\dagger} = -\frac{\hbar\omega_o}{2}\frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & +i \\ +i & 1 \end{bmatrix}$$

$$= -\frac{\hbar\omega_o}{2}\frac{1}{2} \begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix} \begin{bmatrix} 1 & +i \\ -i & -1 \end{bmatrix} = -\frac{\hbar\omega_o}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}$$

Note that the rotated H is no longer diagonal. Regardless, the eigenfunctions of H are the rotated wavefunctions, u, determined above.

$$\mathcal{H}'|u'_{+1/2}> = E_{+1/2}|u'_{+1/2}> = -\frac{\hbar\omega_o}{2} \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix}$$

$$= -\frac{\hbar\omega_o}{2}\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -i \end{bmatrix} = -\frac{\hbar\omega_o}{2}|u'_{+1/2}>$$

180° Rotation: α = π

$$R_x(\pi) = \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$$

Applying this rotation to $u_{+1/2}$:

$$u'_{+1/2} = R_x(\pi)u_{+1/2} = \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ -i \end{bmatrix} = -iu_{-1/2}$$

The 180° rotation completely converts one eigenstate, $u_{+1/2}$, to the other eigenstate, $u_{-1/2}$. This is the expected behavior of a 180° pulse, exchanging the populations of one state for another.

360° Rotation: α = 2π

We expect this rotation to leave any operator or wavefunction unchanged, $R_u(2\pi) = \tilde{1}$, the unity matrix. This result should always be obtained, regardless of the direction of the rotation axis:

$$R_u(2\pi) = \tilde{1}\cos\pi - i\sigma_u\sin\pi = \tilde{1}(-1) = \tilde{1}(-1) = -1\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

The negative sign simply represents a phase shift of the wavefunction and does not change any expectation values.