

APPLICATION OF FLOQUET THEORY IN MULTIPLE QUANTUM MAGIC ANGLE SPINNING EXPERIMENTS

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ABSTRACT. We present a method of applying a combination of Floquet Theory and approximations in order to explain the behavior of a state in magic angle spinning experiments. We start by stating the time dependent nature of the Hamiltonian involved in Schrödinger's equation and using Floquet theory to transform this Hamiltonian to a time-independent *Floquet Hamiltonian*. We also show a numerical method to find the eigenvalues of this transformed Hamiltonian, and how it helps in understanding the basic theory of Multiple Quantum Magic Angle Spinning (MQMAS) experiments.

INTRODUCTION

We begin with Schrödinger's equation, which describes the time evolution of a physical state $|\alpha_0\rangle$ (we are using the Dirac notation here) in quantum mechanics. Using only the axioms of quantum mechanics and first order approximation, it is easy to show that the time evolution operator $U(t)$ of a state $|\alpha_0\rangle$ satisfies the differential equation

$$(0.0.1) \quad \frac{\partial U(t)}{\partial t} = \frac{-i}{\hbar} H(t)U(t)$$

where $\hbar = (\text{Planck's constant})/(2\pi)$ and $H(t)$ is the Hamiltonian operator, which describes the energy of the system. How do we actually try to solve this equation? Of course, we must have some information about $U(t)$ and $H(t)$. We note here that in physical application, both $U(t)$ and $H(t)$ have matrix representations. A good theory for these representations can be found in [1], [2] and [3]. For example, if the state we are considering is a spin-1/2 particle, then the state can be written as an element in a 2-dimensional Hilbert space, and $U(t)$ and $H(t)$ have representations in $su(2)$. By specifying that the state is normalized at all times t , we see that $U(t)$ must be unitary. Moreover, we note that

$$U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0)$$

for $t_0 \leq t_1 \leq t_2$. Physically, this just says that the evolution of a state from time t_0 to t_2 is the same as its evolution from t_0 to some intermediate time t_1 followed by its time evolution from t_1 to t_2 . It follows that $U(t)$ must satisfy

$$\lim_{\partial t \rightarrow 0} U(t_0 + \partial t, t_0) = 1,$$

where 1 represents the identity operator. We see that

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$$U(t_0 + \partial t, t_0) = 1 - \frac{H(t)\partial t}{\hbar}$$

has the required properties, if we assume that $H(t)$ is Hermitian.

1. SOLVING SCHRÖDINGER'S EQUATION

1.1. Time-Independent Hamiltonian. The simplest case that we can consider while trying to solve 0.0.1 is when the Hamiltonian is time-independent. An example of this case is when the state is the spin of a particle in a stationary magnetic field. In this case, the solution to 0.0.1 is given by

$$U(t) = \exp\left(\frac{-i}{\hbar} Ht\right),$$

as can easily be checked by directly substituting in 0.0.1. Note that by using the uniqueness of solutions of partial differential equations, this is the only solution.

1.2. Time-Dependent Hamiltonian. Here, there are two cases we can consider. The easy one is when the Hamiltonian operator is time-dependent and commute at all times t , namely that $H(t)H(t') = H(t')H(t) \forall t, t'$. Here, a solution to 0.0.1 is given by

$$U(t) = \exp\left(\frac{-i}{\hbar} \int_0^t H(s)ds\right).$$

The more interesting case arises when $H(t)$ is time-dependent and $H(t)$'s at different times don't commute. A formal solution in this case is usually given by a *Dyson time series*, which is of the form

$$U(t) = 1 + \sum_{n=1}^{\infty} \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} H(t_1)H(t_2)\dots H(t_n)dt_n.$$

The derivation of this solution is easy, but tedious. We don't present the proof here, but a good reference to this can be found in [1].

2. HAMILTONIAN IN MQMAS EXPERIMENTS

In MQMAS experiments, the Hamiltonian for a spin-3/2 particle in a magnetic field of strength B_1 is given by:

$$\begin{aligned} H(t) &= H_{rf} + H_q(t) \\ &= \frac{\omega_1 S_x}{2} + q(t)(S_z^2 - S^2), \end{aligned}$$

where

$$\omega_1 = -\gamma B_1, q(t) = \frac{\nu_q}{2}(3 \cos^2 \beta - \eta \sin^2 \alpha \cos 2\beta), S^2 = 15E/4,$$

and

$$S_x = \frac{1}{2} \begin{pmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 1 & 0 \\ 0 & 1 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{pmatrix}$$

$$S_z = \frac{1}{2} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}.$$

Here, ν_q is a constant called the quadrupolar frequency, and α is an angle of rotation about the z axis and β is an angle of rotation about the new y axis.

If Q is an observable, then the evolution of its expected value is given by

$$\langle Q \rangle (t) = \text{tr} [QU(t)\sigma(0)U^{-1}(t)]$$

where $\sigma(0)$ is the initial density operator [1]. In MQMAS experiments, the density and the time evolution operators are given by $\sigma(0) = S_z = 3S_z^{1,4} + S_z^{2,3}$ and $Q = S_y^{1,4}$ for MQ transition, where

$$S_z^{1,4} = \frac{1}{2} \begin{pmatrix} 3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 3 \end{pmatrix}$$

$$S_z^{2,3} = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$S_y^{1,4} = \frac{i}{2} \begin{pmatrix} 0 & 0 & 0 & -\sqrt{3} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \sqrt{3} & 0 & 0 & 0 \end{pmatrix}.$$

The observable and the initial density operator can be expressed in terms of spin-1/2 operators by switching bases from $|3/2\rangle, |1/2\rangle, |-1/2\rangle$ and $|-3/2\rangle$ to $1/\sqrt{2}(|3/2\rangle \pm |-3/2\rangle)$ and $1/\sqrt{2}(|1/2\rangle \pm |-1/2\rangle)$. This is done by using the rotation matrix

$$R = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & -1 \\ 1 & 0 & -1 & 0 \end{pmatrix},$$

so that the Hamiltonian becomes block diagonal and the two 2x2 subspaces can be described independently by the spin-1/2 operators:

$$H_R = R^{-1}HR = \frac{1}{2} \begin{pmatrix} q & \sqrt{3}\omega_1 & 0 & 0 \\ \sqrt{3}\omega_1 & -q + 2\omega_1 & 0 & 0 \\ 0 & 0 & q & \sqrt{3}\omega_1 \\ 0 & 0 & \sqrt{3}\omega_1 & -q - 2\omega_1 \end{pmatrix}$$

$$= \begin{pmatrix} H_a & 0 \\ 0 & H_b \end{pmatrix}$$

$$H_a = \omega_1 E + (q(t) - \omega_1) I_z + \sqrt{3}\omega_1 I_x$$

$$H_b = -\omega_1 E + (q(t) + \omega_1) I_z + \sqrt{3}\omega_1 I_x$$

It follows that the time evolution operator is also block diagonal:

$$U_R = \begin{pmatrix} U_a & 0 \\ 0 & U_b \end{pmatrix}$$

Moreover, the density and Q change since $S_x^{1,4}$ gets transformed to $S_z^{1,3}$, $S_y^{1,4}$ to $-S_y^{1,3}$, $S_z^{1,4}$ to $S_x^{1,3}$, etc.

A further modification that eliminates the large quadrupolar coupling constant is achieved by transforming to the so called rotating frame of reference. This is done by using the rotation $R_q = e^{\mp i\phi(t)I_z}$. The changes in $H_a(t)$ and $H_b(t)$ are as follows:

$$(2.0.1) \quad \begin{aligned} H_a &= \omega_1 E - \omega_1 I_z + \frac{\sqrt{3}}{2}\omega_1 [I_+ e^{-i\phi t} + I_- e^{i\phi t}] \\ H_b &= -\omega_1 E + \omega_1 I_z + \frac{\sqrt{3}}{2}\omega_1 [I_+ e^{-i\phi t} + I_- e^{i\phi t}] \end{aligned}$$

where $I_{\pm} = I_x \pm iI_y$. The transformation to the rotating frame causes a phase modulation to the rf term in the Hamiltonian, which can be expanded in a Fourier series as

$$e^{i\phi(t)} = \sum_{n=-\infty}^{\infty} s_n e^{in\omega_r t}.$$

Here $\phi(t) = \int_0^t q(s)ds$ and $\omega_r = 2\pi/\tau$, where τ is the rotor period.

Thus, the spin evolution $S_{ex}(t)$ of a particle can be obtained as

$$S_{ex}(t) = \text{tr}[-S_y^{1,3} U_R(t) (3S_x^{1,3} + S_x^{2,4}) U_R^{-1}(t)].$$

In order to explain the behavior of $S_{ex}(t)$, we need to find U_R . The above step simplifies the problem since we now only have to solve for U_a and U_b , which are time evolution operators associated with the Hamiltonian described in 2.0.1.

3. SOLVING SCHRÖDINGER'S EQUATION USING FLOQUET THEORY

It is not easy to analytically solve 0.0.1 when the Hamiltonian is time dependent and the Hamiltonian at different times do not commute. The above situation in MQMAS experiments is one such case. We however note that the Hamiltonian in this case is periodic with period $\tau = 2\pi/\omega_r$. In this case, we prove Floquet's theorem:

Theorem 3.0.1. *If the Hamiltonian is periodic with period τ , then the solution $U(t)$ of 0.0.1 can be written as*

$$(3.0.2) \quad U(t) = P(t)e^{-iQt}P(0)^{-1}$$

where $P(t)$ is periodic with period τ and Q is time independent.

Proof. We first observe that:

$$\frac{\partial U(t+\tau)}{\partial t} = \frac{-i}{\hbar} H(t)U(t+\tau)$$

Thus, $U(t+\tau)$ also satisfies Schrödinger's equation with the same Hamiltonian. It follows that:

$$\frac{\partial (U^{-1}(t)U(t+\tau))}{\partial t} = \frac{i}{\hbar} \overline{U(t)}^t H(t)U(t+\tau) - \frac{i}{\hbar} \overline{U(t)}^t H(t)U(t+\tau) = 0.$$

Thus,

$$(3.0.3) \quad U^{-1}(t)U(t+\tau) = A$$

where $A = U(\tau)$ is unitary and independent of time. Let B be an operator such that

$$D = B^{-1}AB$$

where D is diagonal and unitary. Since every unitary operator can be written as the exponential of a skew-Hermitian operator, it follows that

$$D = B^{-1}AB = e^{-iQ\tau} \text{ i.e. } A = Be^{-iQ\tau}B^{-1},$$

where Q is diagonal. Hence by 3.0.3, we get

$$U(t+\tau)B = U(t)Be^{-iQt}.$$

It follows that

$$U(t+\tau)Be^{-iQ(t+\tau)} = U(t)Be^{-iQt}.$$

By letting $P(t)$ equal the right hand side of the above equation, we get

$$P(t+\tau) = U(t+\tau)Be^{-iQ(t+\tau)} = U(t)Be^{-iQt} = P(t).$$

This shows that $P(t)$ is periodic with period τ , and since $B = P(0)$, it follows that $U(t)$ has the stated form. \square

The main idea of Floquet theory is to solve for $P(t)$ and Q , and hence solve for $U(t)$. Since both $H(t)$ and $P(t)$ are periodic, they can be written as a Fourier series in $\omega_r = 2\pi/\tau$:

$$H(t) = \sum_{-\infty}^{\infty} H^{(n)} e^{in\omega_r t},$$

$$P(t) = \sum_{-\infty}^{\infty} P^{(n)} e^{in\omega_r t}.$$

Substituting these in Schrödinger's equation, we get

$$\sum_{n=-\infty}^{\infty} iP^{(n)}e^{in\omega_r t} (n\omega_r - Q) e^{-iQt} = - \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} iH^{(n-m)}P^{(m)}e^{in\omega_r t}e^{-iQt}.$$

Comparing coefficients of $e^{in\omega_r t}$ yields

$$P^{(n)}(n\omega_r - Q) = - \sum_{m=-\infty}^{\infty} H^{(n-m)}P^{(m)}$$

which can be rewritten as

$$P^{(n)}Q = \sum_{m=-\infty}^{\infty} \left(H^{(n-m)} + n\omega_r\delta_{mn} \right) P^{(m)}.$$

This looks like an eigenvalue problem with "eigenvalue" Q and "eigenvector" $P(t)$. We immediately note that Q need not be unique. An addition of $n\omega_r$ to Q also gives a solution. However, it is easy to see that these are the only ones.

In matrix notation, we can write this as

$$P_{ru}^{(n)}Q_{uu} = \sum_s \sum_{m=-\infty}^{\infty} \left(H_{rs}^{(n-m)} + n\omega_r\delta_{mn}\delta_{rs} \right) P_{su}^{(m)}.$$

So we get a new Hamiltonian operator $H^{\mathcal{F}}$, called the Floquet Hamiltonian, that has double indexing: The indices r, s and u from the Hilbert space, and the Fourier indices n, m . A more complete treatment of this theory can be found in [4].

$$H^{\mathcal{F}} = \begin{pmatrix} \dots & H^{(2)} & H^{(3)} & H^{(4)} & H^{(5)} \\ H^{(0)} + 2\omega_r & H^{(1)} & H^{(2)} & H^{(3)} & H^{(4)} \\ H^{(-1)} & H^{(0)} + \omega_r & H^{(1)} & H^{(2)} & H^{(3)} \\ H^{(-2)} & H^{(-1)} & H^{(0)} & H^{(1)} & H^{(2)} \\ H^{(-3)} & H^{(-2)} & H^{(-1)} & H^{(0)} - \omega_r & H^{(1)} \\ H^{(-4)} & H^{(-3)} & H^{(-2)} & H^{(-1)} & H^{(0)} - 2\omega_r \\ H^{(-5)} & H^{(-4)} & H^{(-3)} & H^{(-2)} & \dots \end{pmatrix}$$

Q_{uu} are the eigenvalues of the Floquet matrix with eigenvectors $P_{su}^{(m)}$.

Thus, we have reduced the problem from computing a time-dependent Hamiltonian to computing a time-independent Hamiltonian.

How does this help in solving for $P(t)$ and Q ? In the case that we have considered where the Hamiltonians are given by 2.0.1, the Floquet Hamiltonians obtained by transforming $H_a(t)$ and $H_b(t)$ are

$$H_{a,b}^{\mathcal{F}} = \begin{pmatrix} \begin{pmatrix} \dots & 0 & 0 & 0 & 0 \\ 0 & \omega_r & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\omega_r & 0 \\ 0 & 0 & 0 & 0 & \dots \end{pmatrix} & c \begin{pmatrix} \dots & s_1 & s_2 & s_3 & s_4 \\ s_{-1} & s_0 & s_1 & s_2 & s_3 \\ s_{-2} & s_{-1} & s_0 & s_1 & s_2 \\ s_{-3} & s_{-2} & s_{-1} & s_0 & s_1 \\ s_{-4} & s_{-3} & s_{-2} & s_{-1} & \dots \end{pmatrix} \\ c \begin{pmatrix} \dots & \bar{s}_1 & \bar{s}_2 & \bar{s}_3 & \bar{s}_4 \\ \bar{s}_{-1} & \bar{s}_0 & \bar{s}_1 & \bar{s}_2 & \bar{s}_3 \\ \bar{s}_{-2} & \bar{s}_{-1} & \bar{s}_0 & \bar{s}_1 & \bar{s}_2 \\ \bar{s}_{-3} & \bar{s}_{-2} & \bar{s}_{-1} & \bar{s}_0 & \bar{s}_1 \\ \bar{s}_{-4} & \bar{s}_{-3} & \bar{s}_{-2} & \bar{s}_{-1} & \dots \end{pmatrix} & \begin{pmatrix} \dots & 0 & 0 & 0 & 0 \\ 0 & \pm\Omega_1 & 0 & 0 & 0 \\ 0 & 0 & \Omega_0 & 0 & 0 \\ 0 & 0 & 0 & \pm\Omega_{-1} & 0 \\ 0 & 0 & 0 & 0 & \dots \end{pmatrix} \end{pmatrix}$$

where the \pm stand for the transformations in $H_a(t)$ and $H_b(t)$ respectively, $\pm\Omega_n = n\omega_r \pm \omega_1$ and $c = \sqrt{3\omega_1}/2$. We should observe here that the Hilbert space index and the Fourier index have been swapped here. The technique that we use to "diagonalize" this Hamiltonian is by using the so called Jacobi transformations. These are described in [5].

$$J_{mn} = \begin{pmatrix} \dots & \dots & \dots & \dots & \dots \\ \dots & 1 & \dots & r_{m-n} & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & -\bar{r}_{m-n} & \dots & 1 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

and are used numerically to eliminate the off-diagonal elements. In the case of $H_a(t)$, each application of the Jacobi transformation changes the diagonal elements $n\omega_r$ and $n\omega_r + \omega_1$ of the Floquet Hamiltonian by

$$\delta_a = -\text{sign}(k\omega_r + \omega_1) \sqrt{(k\omega_r + \omega_1)^2 + 3\omega_1^2 |s_{-k}|^2}.$$

By successively applying these transformations, we can approximately diagonalize $H^{\mathcal{F}}$. The total change in the diagonal element $n\omega_r$ and $n\omega_r + \omega_1$ is

$$\Delta_a = -\sum_{k=-\infty}^{\infty} \text{sign}(k\omega_r + \omega_1) \sqrt{(k\omega_r + \omega_1)^2 + 3\omega_1^2 |s_{-k}|^2}.$$

Note that the new values of 0 and ω_1 in $H^{\mathcal{F}}$ after diagonalizing give the diagonal entries of Q . Since we know that Q is diagonal, we get one possible value of Q , namely

$$Q_{0,a} = \begin{pmatrix} \Delta_+/2 & 0 \\ 0 & \omega_1 - \Delta_+/2 \end{pmatrix}.$$

As observed before, Q is not unique, but the other possible values of Q are $Q_{0,a} + n\omega_r$. Furthermore, this also allows us to solve for $P(t)$:

$$P_a(t) = \sum_{k=-\infty}^{\infty} (2\delta_{k0}E + r_{k+}I_- - \bar{r}_{k+}I_+) e^{ik\omega_r t}$$

where $r_{k+} = \delta_a/(\sqrt{3\omega_1}s_{-k})$ and $I_{\pm} = I_x \pm iI_y$.

The same procedure can be applied to $H_b(t)$ to obtain the corresponding $Q_{0,b}$ and $P_b(t)$:

$$Q_{0,b} = \begin{pmatrix} \Delta_b/2 & 0 \\ 0 & -\omega_1 - \Delta_b/2 \end{pmatrix}$$

$$P_b(t) = \sum_{k=-\infty}^{\infty} (2\delta_{k0}E + r_{k-}I_- - \bar{r}_{k-}I_+) e^{ik\omega_r t}$$

where

$$\Delta_b = - \sum_{k=-\infty}^{\infty} \text{sign}(k\omega_r - \omega_1) \sqrt{(k\omega_r - \omega_1)^2 + 3\omega_1^2 |s_{-k}|^2}.$$

We further note that

$$P_{a,b}(0)^{-1} = \sec\left(\frac{\theta_{\pm}}{2}\right) R$$

where

$$R_{\pm} = e^{-iI_z \phi_{\pm}} e^{-iI_y \theta_{\pm}} e^{iI_z \phi_{\pm}}$$

and the angles ϕ_{\pm} and θ_{\pm} are defined by

$$e^{i\phi_{\pm} \tan\left(\frac{\theta_{\pm}}{2}\right)} = \sum_k \bar{r}_{k\pm}.$$

We are thus able to solve for the time evolution operator $U(t)$ by using 3.0.2.

$$U_{a,b}(t) = \left(\sum_{k=-\infty}^{\infty} (2\delta_{k0}E + r_{k\pm}I_+ - \bar{r}_{k\pm}I_-) \sec\left(\frac{\theta_{\pm}}{2}\right) e^{i(k\omega_r \mp \omega_1/2)t} \right) e^{-i(\Delta_{a,b} \mp \omega_1)I_z t} R.$$

We end with a graph shown in Fig.1 of how numerical simulations of $S_{ex}(t)$ compared with the Floquet theory method.

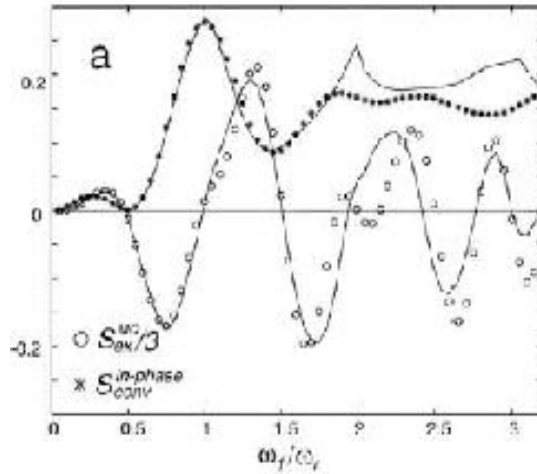


Fig.1

The smooth lines are the ones that are obtained using the Floquet theory method and the circles are the computer simulated values of $S_{ex}(t)$. We note that there is a close match between the two for small values of ω_1/ω_r . However, due to the approximations used by the Jacobi transformations, the values differ as ω_1/ω_r becomes large.

What are the directions that we can proceed in with the ideas presented here? One of the things we can do is to try and use perturbation theory and see if we can improve on the numerical method used in the end. Another thing to note is that the Hamiltonian $H_q(t)$ in section 2 is described only up to first order. As NMR instruments become more sophisticated, higher order effects may be observable. An interesting thing to look forward to is to see what theory will be required to explain these effects. I am already working on the theory of these higher order quadrupolar effects with Dr John Quine and Dr Zhehong Gan.

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REFERENCES

1. Sakurai J.J, *Modern Quantum Mechanics*, Addison-Wesley, 1994.
2. Rose M.E, *Elementary Theory of Angular Momentum*, John Wiley and Sons, 1957.
3. Sternberg S, *Group Theory and Physics*, Cambridge University Press, 1994.
4. Levante T.O, Baldus M, Meier B.H, and Ernst R.R, *Formalized quantum mechanical Floquet theory and its application to sample spinning in nuclear magnetic resonance*, Mol. Phys. **86** (1995), no. 5, 1195–1212.
5. Press W.H, Teukolsky S.A, Vetterling W.T, and Flannery B.P, *Numerical Recipes in C*, Cambridge University Press, 1988.
6. Gan Z and Grandinetti P.J, *Rotary Resonance in Multiple-Quantum Magic-Angle Spinning*, preprint.