

# Applications of Linear Algebra to Chemical Exchange Nuclear Magnetic Resonance

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## I. ABSTRACT

In this paper we explore key linear algebra tools for understanding the impact of chemical exchange on spin dynamics in nuclear magnetic resonance (NMR). We demonstrate matrix representations of the Hamiltonian, relaxation, and chemical exchange super-operators in Liouville space and apply these matrices to simulate a low magnetic (0-20mT) field NMR spectra for the  $\text{NH}_3$  and  $\text{NH}_4^+$  equilibrium system. This paper is mainly based on the article *Essential tools of linear algebra for calculating nuclear spin dynamics of chemically exchanging systems* [1].

## II. ATTRIBUTION

Sudarshan worked on the Abstract, Introduction, subsections Mathematical Formulation *H-L*, *Q*, and the Discussion and Conclusions. Ethan worked on the Examples and Numerical Results and the subsections Mathematical Formulation *A-G*. Jerry worked on Examples and Numerical Results, subsections of Mathematical Formulation *M-P*, *R*, and Discussion and Conclusions.

## III. INTRODUCTION

### A. Theory of NMR

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful and versatile analytical technique extensively utilized in various scientific domains such as medicine, biochemistry, physics, industry, and more. It exploits the unique magnetic properties of certain atomic nuclei, making it an invaluable tool in studying molecular structures and dynamics.

The fundamental principle of NMR lies in the behavior of certain atomic nuclei when exposed to an external magnetic field. At the heart of NMR spectroscopy is the concept of nuclear spin states. These states are specific to certain nuclei which, when placed in an external magnetic field, can occupy various energy levels. The NMR technique primarily detects transitions between these spin states, offering insights that are specific to the type of nucleus and its chemical environment. However, it's crucial to note that NMR spectroscopy is effective only for nuclei with a non-zero nuclear spin ( $I \neq 0$ ). Nuclei that have a spin value of zero are effectively 'invisible'

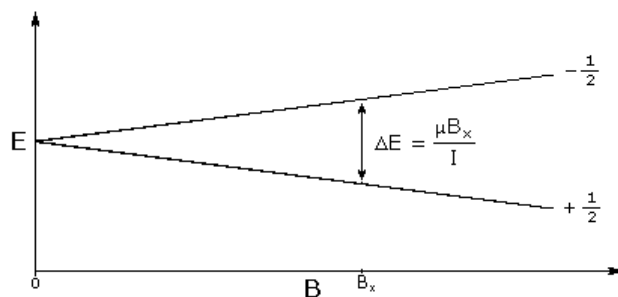


Fig. 1. The Difference in Energy between two spin states over a varying magnetic field B

to NMR, limiting the technique's applicability to certain types of atoms [3].

The theoretical underpinnings of NMR are rooted in quantum mechanics, particularly the intrinsic spin of the nucleus, denoted by the quantum number  $S$ . A key aspect of this theory is the relationship between the nuclear spin and the magnetic moment  $\mu$  of the nucleus, encapsulated in the equation  $\mu = \gamma \cdot S$ . Here,  $\gamma$  represents a non-zero constant, tying the magnetic moment directly to the spin. It is known as the gyromagnetic ratio. This relationship is fundamental to NMR, as it is the magnetic moment that interacts with the external magnetic field, making the NMR observation possible. Because of this nuclei whose quantum spin is zero cannot be measured using NMR. Isotopes with an even number of protons and neutrons have no magnetic moment and thus cannot be measured using NMR [3].

In practical terms, when a nucleus with a spin of  $I = 1/2$  is subjected to an external magnetic field ( $B$ ), it can exist in two spin states:  $+1/2$  and  $-1/2$ . The energy difference between these states in a specific magnetic field ( $B_x$ ) is given by the equation:  $E = \mu \frac{B_x}{I}$ . This difference is generally very slight, necessitating the use of strong magnetic fields in NMR to distinguish these energy states more clearly. Typically, the resonance frequencies used in NMR under these conditions fall within the radio frequency range, which is critical for the practical implementation of NMR spectroscopy [3].

A distinguishing feature of NMR is its ability to differentiate between various elements and isotopes. This specificity stems from the fact that each type of nuclide absorbs energy at a

distinct frequency. Consequently, NMR can target specific isotopes, leading to various specialized forms of NMR such as  $^1\text{H}$  NMR (proton NMR),  $^{15}\text{N}$  NMR (nitrogen NMR),  $^{13}\text{C}$  NMR (carbon NMR), and  $^{31}\text{P}$  NMR (phosphorus NMR), among others. This selectivity is incredibly valuable in analyzing complex molecular structures and dynamics [3].

Another critical concept in NMR is nuclear shielding. This phenomenon occurs when the electrons surrounding a nucleus modify the local magnetic field at the nucleus. This alteration, generally a reduction in the magnetic field, is due to the electron cloud's influence and is known as nuclear shielding. This effect allows NMR to be a powerful tool in identifying molecular structures. In different chemical environments, nuclei of the same type will experience varying degrees of shielding. This variation in shielding, observable as a difference in the surrounding magnetic field, is referred to as the chemical shift. The chemical shift is a fundamental parameter in NMR spectroscopy, providing detailed information about the electronic environment of the nucleus and thus insights into molecular structure and interactions [3].

The final relevant concept to NMR is J-couplings, also known as spin-spin coupling or indirect dipole-dipole coupling; they play a pivotal role in nuclear chemistry and nuclear physics. This phenomenon occurs due to the hyperfine interactions between nuclear spins and local electrons, mediated through chemical bonds connecting these spins. Essentially, it is an indirect interaction between two nuclear spins. One of the key features of J-coupling is that it contains valuable information about the molecular structure. By analyzing J-coupling in NMR spectroscopy, scientists can infer relative bond distances and angles within molecules. This aspect is crucial for understanding the three-dimensional structure and connectivity of chemical bonds in various compounds. Most importantly, J-coupling is instrumental in providing insights into the connectivity of chemical bonds. This information is fundamental for chemists and physicists in deciphering the molecular structure and understanding the behavior of molecules under various conditions. The presence of J-coupling is often indicated by the complex splitting patterns observed in the NMR spectra of even relatively simple molecules. These splitting patterns, or multiplets, arise due to the interactions between different sets of equivalent or non-equivalent nuclei within a molecule.

### B. Impacts of Chemical Exchange

Chemical exchange describes molecular motion involving changes in binding conformation which leads to alterations in an NMR spectroscopy graph; this makes it difficult to interpret spectra and extract information about molecular structure. In this paper we detail the linear algebra tools for calculating nuclear spin dynamics using density operator formalism by constructing matrix representations of the necessary operators in Hilbert and Liouville spaces. We will describe a full spin dynamical evolution of the system subject to the chemical exchange reaction [1].

The differential equations describing the chemical kinetics (the rate of change of the concentration of the molecules as a function of time) of the systems is written in matrix form

$$\begin{aligned} \frac{d}{dt} \begin{pmatrix} [A] \\ [AB] \end{pmatrix} &= \begin{pmatrix} -k_a[B] & k_d \\ k_a[B] & -k_d \end{pmatrix} \begin{pmatrix} [A] \\ [AB] \end{pmatrix} \\ &= \begin{pmatrix} -\tilde{k}_a & +k_d \\ +\tilde{k}_a & -k_d \end{pmatrix} \begin{pmatrix} [A] \\ [AB] \end{pmatrix} \end{aligned} \quad (1)$$

Where  $[A]$ ,  $[B]$ , and  $[AB]$  represent the concentrations of molecules A, B, AB and  $\tilde{k}_a = k_a[B]$ .

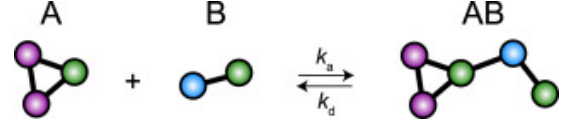


Fig. 2. Dissociation of arbitrary molecules A and B

This equation however, only works when the spin state of the molecule B is not changing with time; examples of a time-independent spin state of B include SABRE experiments or if B can be considered depolarized as is the case for  $H^+$  exchanging with ammonia.

We will now describe the spin dynamics of a chemically exchanging system in Liouville Space (the space of quantum mechanical operators) instead of the Hilbert space (space of quantum mechanical states). This is advantageous when considering that the relaxation and chemical exchange superoperators need only be calculated once. In the absence of chemical exchange the spin dynamics of a dissociating molecule  $i = (A \rightarrow AB)$  is described by the Liouville-Von Neumann equation:

$$\frac{d}{dt} \hat{\rho}_i = \hat{L}_i \hat{\rho} \quad (2)$$

Where  $\rho$  represents the density operator corresponding to the molecule  $i$ .

The Liouvillian superoperator,

$$\hat{L}_i = -i\hat{H}_i + \hat{R}_i \quad (3)$$

acts on  $\rho_i$  and describes both coherent evolution dictated by the Hamiltonian superoperator  $\hat{H}_i = [\hat{H}_i, \cdot]$  and the incoherent relaxation represented by the relaxation superoperator  $\hat{R}_i$  of the nuclear spins within the molecule.

In this context coherent evolution refers to the orderly and predictable change in the state of a quantum system over time, governed by the principles of quantum mechanics and incoherent relaxation often refers to the process by which the orientation of spins or magnetic moments in a material lose their coherence over time. This can be due to various interactions with the environment, like thermal fluctuations or

interactions with other spins. This type of relaxation leads to the decay of magnetization or spin polarization in a material.

We further describe how these superoperators interact with the density operator in Hilbert space in the Mathematical Formulation.

We base our discussion for the formulation of chemical exchange operators on the following assumptions

- 1) Individual events of association and dissociation occurs much faster than nuclear spin dynamics
- 2) The state of molecule B remains unchanged
- 3) Chemical kinetic rates are independent of the nuclear spin degrees of freedom.

#### IV. MATHEMATICAL FORMULATION

##### A. Bra-ket Notation

Bra-ket notation, also referred to as Dirac notation, is a commonly used complex vector simplification used to summarize quantum state arithmetic [4]. A ket describes at its base level a column vector (4)  $\vec{A} = |A\rangle \in \mathcal{H}$  ( $\mathcal{H}$ : Hilbert space described in IV-B). Abstracted, a ket is either a definite state that some quantum effected object is in, or it is a quantum state which is a linear product of multiple states known as superposition. Written as  $|\psi\rangle = c_1|L_1\rangle + c_2|L_2\rangle + \dots + c_n|L_n\rangle$ .

$$|A\rangle = \begin{bmatrix} a_1 \\ \vdots \\ a_n \end{bmatrix} \quad (4)$$

Importantly, the definite state  $|L_2\rangle$  describes some definite observable state like Energy ( $|E_1\rangle, \dots, |E_N\rangle$ ) or Momentum ( $|L_1\rangle, \dots, |L_N\rangle$ ). However, the amount of states may be infinite. For properties like Momentum or position ( $|X_1\rangle, \dots, |X_N\rangle$ ) the states are continuous; making the linear product that produces the quantum state an integral (6) where the wave function  $\psi(x)$  represents the coefficients. The quantum state idealistically represents everything about the particle, so it is the same quantum state that is produced from a linear product of each of the separate observable states. The quantum state represents a superposition of all possible states of all observable values.

$$|\psi\rangle = \sum_{i=0}^n c_i |E_i\rangle \quad (5)$$

$$|\psi\rangle = \int \psi(x) |L_i\rangle \quad (6)$$

It is important to note when looking at spin systems, like in our case, they will be defined in a simplified finite dimensional Hilbert space. That is not idealist and represents only certain features.

In contrast bras  $\langle B|$  are row vectors (7). They are a part of the dual space of the Hilbert space described in IV-B  $\langle\psi| \in \mathcal{H}^*$ , where  $\mathcal{H}^* : \mathcal{H} \rightarrow \mathbb{R}$ . This develops to  $\langle A|B\rangle \in \mathbb{R}$  representing an inner product between  $|A\rangle$  and  $\langle B|$  which, generally in quantum mechanics, evaluates into the traditional hermitian dot product between  $\langle \tilde{A}, \tilde{B} \rangle$ , where the bra is anti linear and the ket is linear.

$$\langle B| = [b_1 \quad \dots \quad b_n] \quad (7)$$

This idea leads to each ket state having a corresponding bra state (8) that is its complex conjugate transpose. So that  $\langle A|A\rangle$  represents the magnitude over the hermitian norm  $\|A\|^2$ . For example take  $\tilde{A} = |A\rangle$

$$\overline{(\tilde{A})}^T = \langle A| \quad (8)$$

##### B. Hilbert space

A Hilbert space generally is a vector space with a defined inner product that is Cauchy complete. This is key when representing quantum states, as it allows for infinite dimensional matrices and therefore bases. Essentially, Cauchy complete means there are no missing elements in or at the boundary of the vector space. Whereas, a more traditional vector space would not include the boundaries that are reachable in infinite linear combinations [5]. This is true for instance in examples of continuous bases like seen for position kets.

$$|\psi\rangle = \int \psi(x) |L_i\rangle \in \mathcal{H} \quad (9)$$

In quantum mechanics Hilbert spaces are used to define a space of possibles states of a given quantum affected object. Each basis vector of the space defines a discrete ket state. Therefore, the linear product as described above creates a quantum state  $\psi$ . Importantly, the coefficients of this linear product represent the probability of the related state occurring where  $|c_n|^2 = p_1$  (assuming properly normalized states). The overall  $|\psi\rangle$  represents a superposition that might collapse into one of the given states.

##### C. Operators

Operators over a Hilbert space represent measurables such as momentum, energy, position. Generally, these map  $\hat{O} : \mathcal{H} \rightarrow \mathcal{H}$ , where the eigenvectors of the operators' matrix form represent the discrete kets of a quantum state. The corresponding Eigenvalues represent the measurable amount of the given quantity [5]. Given a complete angular momentum operator in the x direction  $\hat{I}_x$  over some quantum state  $|\psi\rangle$  with some discrete  $n$  momentum kets  $|L_{1x}\rangle, \dots, |L_{nx}\rangle$  we write

$$|\psi\rangle = c_1|L_{1x}\rangle + \dots + c_n|L_{nx}\rangle \quad (10)$$

To find the eigenvectors:

$$\begin{aligned} (\hat{I}_x - I\lambda)x &= 0 \\ \rightarrow \lambda_1 \dots \lambda_n \\ \vec{\lambda}_n &= \ker(\hat{I}_x - \lambda_n) \\ \rightarrow \vec{\lambda}_1 \dots \vec{\lambda}_n \end{aligned} \quad (11)$$

Therefore:

$$\begin{aligned} \vec{\lambda}_1 &= |L_{1x}\rangle, \dots, \vec{\lambda}_n = |L_{nx}\rangle \\ |\psi\rangle &= c_1 \vec{\lambda}_1 + \dots + c_n \vec{\lambda}_n \end{aligned} \quad (12)$$

This connects to the idea of collapse. A certain quantum state in superposition collapses to some  $k$  state when a measurement is taken. Therefore:

$$|\psi\rangle = \vec{\lambda}_k \text{ (under normalized conditions } c_k = 1) \quad (13)$$

Then when the operator acts on the state it returns to a scaled eigenstate.

$$\hat{I}_x |\psi\rangle = \lambda_k \vec{\lambda}_k \quad (14)$$

$\lambda_k$  is the measured angular momentum of the particle, but  $|\psi\rangle$  is collapsed to an angular momentum state in the x-direction. Therefore, another angular momentum operator in the z-direction cannot produce understandable scaled results. For the angular momentum operator in the z-direction to produce an understandable scaled result, it must first collapse into an eigenstate of the z-operator. However, if this happens the measurement in the x-direction would be lost and it would return to a superposition in the x-direction. If the operators commute (share eigenvectors), then they can operate on the same collapsed state.

This idea encapsulates the key idea of measurement collapse and is vital to understand the roles of operators in quantum mechanics.

#### D. Kronecker Product

The Kronecker product, also called the matrix outer product, is a form of matrix multiplication critical to quantum mechanics. Take for example

$$\exists A \in R^{n \times m}, \exists B \in R^{p \times q} \quad (15)$$

Then, the Kronecker product  $A \otimes B$  follows:

$$A \otimes B \in R^{mp \times nq} \quad (16)$$

this evaluates in block matrix form to

$$A \otimes B = \begin{bmatrix} a_{11}B & a_{12}B & \dots & a_{1n}B \\ a_{21}B & a_{22}B & \dots & a_{2n}B \\ \vdots & \vdots & \ddots & \vdots \\ a_{m1}B & a_{m2}B & \dots & a_{mn}B \end{bmatrix} \quad (17)$$

and expands traditionally to (18) from [7]

The outer product (Kronecker Product), like the inner product, is bi-linear and associative:

$$\begin{aligned} A \otimes (B + C) &= A \otimes B + A \otimes C \\ (B + C) \otimes A &= B \otimes A + C \otimes A \\ (dA) \otimes A &= A \otimes (dB) = k(A \otimes B) \\ (A \otimes B) \otimes C &= A \otimes (B \otimes C) \end{aligned} \quad (19)$$

If an inner product  $(\cdot)$  is defined between  $A, B, C, D$  then

$$(A \otimes B) \cdot (C \otimes D) = (A \cdot B) \otimes (C \cdot D) \quad (20)$$

(due to the mixed-product property).

To form density operators of composite systems, we take the Kronecker product of the density operators linked to each subsystem.

The Kronecker product can also be applied in translation of linear operators from Hilbert space to corresponding super-operators in Louisville space. Additionally, the Kronecker product allows quantum states to be made from composite systems where. Density operators that describe probability of the combined states like  $\mathcal{H} \otimes \mathcal{H}$  will be explored in the next section.

#### E. The Hilbert spaces associated with nuclear spins of molecules

Nuclei like protons and  $N^{15}$  have fractional values of spin and two distinct states. When looking at protons they can either have  $+\frac{1}{2}$  or  $-\frac{1}{2}$  spin. This leads to our construction of a two-dimensional Hilbert space modeling spin where  $\alpha$  represents spin up ( $\frac{1}{2}$ ) and  $\beta$  represents spin down ( $-\frac{1}{2}$ ). We create such a model for a proton as follows

$$|\psi\rangle = c_\beta |\beta\rangle + c_\alpha |\alpha\rangle \quad (21)$$

where  $|\beta\rangle$  and  $|\alpha\rangle$  form a basis for the  $\mathcal{H}$ .

Molecules with several nuclei then have a total Hilbert space associated with the Kronecker product of their individual spaces. For instance given a molecule containing 2 nuclei notated above as X and Y with properties notated as  $\psi$  Their respective Hilbert spaces will be referred as  $\mathcal{H}_X$  and  $\mathcal{H}_Y$ . Then the combined Hilbert space can be given as follows:

$$\mathcal{H}_{XY} = \mathcal{H}_X \otimes \mathcal{H}_Y \quad (22)$$

$$\mathcal{H}_{YX} = \mathcal{H}_Y \otimes \mathcal{H}_X \quad (23)$$

where the relative order of each spin Hilbert space does matter. If the molecule comes associated with the space  $\mathcal{H}_{XY}$  (22) it will be denoted XY, and as YX if it comes associated with space  $\mathcal{H}_{YX}$  (23). Additionally,  $\mathcal{H}_Y$  can be used to represent the previous combination of other multi nuclei molecular fragments. This construction of a total Hilbert space is key for super-operators in chemical exchanging systems.

This idea of a combining spaces is also applicable to individual basis States (kets). For instance in an XY molecule, one of the

$$\begin{bmatrix}
a_{11}b_{11} & a_{11}b_{12} & \cdots & a_{11}b_{1q} & \cdots & \cdots & a_{1n}b_{11} & a_{1n}b_{12} & \cdots & a_{1n}b_{1q} \\
a_{11}b_{21} & a_{11}b_{22} & \cdots & a_{11}b_{2q} & \cdots & \cdots & a_{1n}b_{21} & a_{1n}b_{22} & \cdots & a_{1n}b_{2q} \\
\vdots & \vdots & \ddots & \vdots & \ddots & \ddots & \vdots & \vdots & \ddots & \vdots \\
a_{11}b_{p1} & a_{11}b_{p2} & \cdots & a_{11}b_{pq} & \cdots & \cdots & a_{1n}b_{p1} & a_{1n}b_{p2} & \cdots & a_{1n}b_{pq} \\
\vdots & \vdots & \ddots & \vdots & \ddots & \ddots & \vdots & \vdots & \ddots & \vdots \\
\vdots & \vdots & \ddots & \vdots & \ddots & \ddots & \vdots & \vdots & \ddots & \vdots \\
a_{m1}b_{11} & a_{m1}b_{12} & \cdots & a_{m1}b_{1q} & \cdots & \cdots & a_{mn}b_{11} & a_{mn}b_{12} & \cdots & a_{mn}b_{1q} \\
a_{m1}b_{21} & a_{m1}b_{22} & \cdots & a_{m1}b_{2q} & \cdots & \cdots & a_{mn}b_{21} & a_{mn}b_{22} & \cdots & a_{mn}b_{2q} \\
\vdots & \vdots & \ddots & \vdots & \ddots & \ddots & \vdots & \vdots & \ddots & \vdots \\
a_{m1}b_{p1} & a_{m1}b_{p2} & \cdots & a_{m1}b_{pq} & \cdots & \cdots & a_{mn}b_{p1} & a_{mn}b_{p2} & \cdots & a_{mn}b_{pq}
\end{bmatrix} \quad (18)$$

basis states could be described as the Kronecker product of the basis states of their composite Hilbert spaces. This would be written as

$$|ij\rangle_{XY} = |i\rangle_X \otimes |j\rangle_Y \quad (24)$$

Here,  $|i\rangle_X$  denotes a Zeeman basis state for the nucleus X, and  $|j\rangle_Y$  signifies a Zeeman basis state for the nucleus Y. A Zeeman basis refers to a set of quantum states that are eigenstates of the spin component in the direction of an external magnetic field. The entire collection of basis states within the multi nuclei Hilbert space encompasses all conceivable combinations of Zeeman basis states—each linked to a specific nuclear spin of each nuclei or molecular fragment.

The Zeeman product basis allows for the targeted manipulation of individual spins, offering distinct advantages in constructing chemical exchange super-operators. Throughout this paper, we consistently use this basis for representing a diverse array of operators essential for the simulation.

#### F. Matrix representations of angular momentum operators

In specific we will be looking at operators of the angular momentum that arises from the spin of these nuclei to lead us to calculate the NMR. First we analyse the operators for a single nuclei system with  $\frac{1}{2}$  spin. Working in a 3D we will have 3 operators for each dimension  $\hat{I}_x$ ,  $\hat{I}_y$ ,  $\hat{I}_z$ . The matrix forms of each of these operators in a Zeeman basis are as follows:

$$\begin{aligned}
\hat{I}_x &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\
\hat{I}_y &= \frac{1}{2i} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \\
\hat{I}_z &= \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\end{aligned} \quad (25)$$

where, as explained above their respective eigenvectors represent the distinct basis states in a Hilbert Space of spin. Here, the eigenvalues represent the value of the angular momentum associated with the spin.

When looking at multi nuclei (multi- $\frac{1}{2}$ spin) systems, the spin angular momentum operators can now be formed by taking the Kronecker product between the operators of multiple single-spins and the identity operators. Identity operators are just operator that do nothing in 2x2 this is just I.

Let  $\hat{I}_{i\alpha}$  denote the  $\alpha$ -component of the angular momentum operator in reaction to some  $i$ -th spin. So in Zeeman basis the  $\hat{I}_{i\alpha}$  is defined as follows:

$$\hat{I}_{i\alpha} = 1_{i-1} \otimes \hat{I}_{\alpha} \otimes 1_{n-1} \quad (26)$$

where  $\hat{1}_k$  depicts the identity matrix size  $2^k \times 2^k$ . To ensure compatibility.

For instance, the  $\hat{I}_{2z}$  giving the z component for the second spin of a three-spin -1/2 system would be described as:

$$\hat{I}_{2z} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (27)$$

#### G. Matrix representations of Hamiltonian operators

In quantum mechanics we use what is known as a Hamiltonian operator to represent the total energy. It is commonly expressed as the sum of operators corresponding to kinetic and potential energy  $\hat{H} = \hat{T} + \hat{V}$ . One of its most recognizable uses is as the operator in the right hand side of the Schrodinger equation.

When deriving a Hamiltonian operator for some quantum system with a known momentum operator it is generally proportional to the momentum operator squared  $\hat{I}^2$ . This will be seen below in our derivation of the Hamiltonian operator for use in Calculating NMR.

**1) Zero-field Hamiltonian:** We are specifically analysing the NMR in a zero field (B-field). Thus, we are not concerned with any external potentials effecting the molecules. Instead we are concerned with the with chemical J-couplings between spins.

We calculate the operator as follows where  $J_{ij}$  represents the  $j$ -coupling term between  $i$ -th and  $j$ -th spins.

$$\hat{H} = \sum_{i < j} J_{ij} (\hat{I}_i \cdot \hat{I}_j) \quad (28)$$

Because we are using the Zeeman bases for the angular momentum as defined in (25), the Hamilton operator instead takes the below form:

$$H = \sum_{i < j} J_{ij} \left( \sum_{\alpha=x,y,z} I_{i\alpha} I_{j\alpha} \right) \quad (29)$$

where  $\hat{I}_{i\alpha}$  is built as defined in IV-F

#### H. Matrix representations of density operators in Hilbert space

In Hilbert space, the density operator is represented as a square matrix and is denoted  $\hat{\rho}$ . It can be expanded over the basis vectors for the Hilbert space  $[|i\rangle]$  as:

$$\hat{\rho} = \sum_{ij}^d \rho_{ij} |i\rangle \langle j|. \quad (30)$$

In this context, the  $d$  denotes the dimension of the density operator, while  $\rho_{ij}$  are the individual elements that constitute the density matrix with respect to a specified basis set. The matrix form of the density operator, when expressed in this particular basis, can be articulated as follows:

$$\begin{pmatrix} \rho_{11} & \cdots & \rho_{1d} \\ \vdots & \ddots & \vdots \\ \rho_{d1} & \cdots & \rho_{dd} \end{pmatrix},$$

where  $\rho_{ij}$  is placed at the  $i$ -th row and the  $j$ -th column in the matrix.

The matrix representation of the concentration normalized density operator is obtained by element wise multiplication of the corresponding density matrix by the concentration.

#### I. The action of superoperators in Hilbert space

The action of a superoperator  $\hat{\hat{O}}$  on an operator  $\hat{A}$  can be expressed as a linear combination of the transformations involving the operators  $\hat{M}_k$  and  $\hat{N}_l$  and the associated coefficients  $o_{kl}$ :

$$\hat{\hat{O}}\hat{A} = \sum_{kl} o_{kl} \hat{M}_k \hat{A} \hat{N}_l \quad (31)$$

There are similarities in the definitions between operators and superoperators. Operators describe transformations between quantum states, while superoperators describe transformations between operators that act on the quantum states. In the same that operators are represented as matrices in Hilbert space,

which is spanned by the quantum states, superoperators can also be represented by matrices in a higher-dimensional super-space known as Liouville space.

In Liouville space, the basis vectors are linear operators rather than quantum states. In the following, we discuss the matrix representation of operators and superoperators in Liouville space.

#### J. Matrix representations of density operators in Liouville space

The mapping of a density operator from Hilbert space into Liouville space involves the transformation:

$$\hat{\rho} = \sum_{i,j} \rho_{ij} |i\rangle \langle j| \longrightarrow |\rho\rangle\rangle = \sum_{ij} \rho_{ij} |ij\rangle\rangle,$$

where the basis operator  $(|i\rangle \langle j|)$  in Hilbert space is transformed into the basis state  $|ij\rangle\rangle$  in Liouville space. The mapped density operator is denoted by  $|\rho\rangle\rangle = |i\rangle \otimes |j\rangle$ .

As a result, the density operator in Liouville space is represented as a vector by “flattening” its matrix representation in Hilbert space. This is done in a row-wise manner, which means we concatenate the rows of the matrix to obtain a column-vector:

$$\begin{pmatrix} \rho_{11} & \cdots & \rho_{1d} \\ \vdots & \ddots & \vdots \\ \rho_{d1} & \cdots & \rho_{dd} \end{pmatrix} \longrightarrow \begin{pmatrix} \rho_{11} \\ \rho_{12} \\ \vdots \\ \rho_{1d} \\ \vdots \\ \rho_{dd} \end{pmatrix}. \quad (32)$$

Here a  $d \times d$  density matrix is reshaped into a column vector of dimension  $d^2 \times 1$ , where  $d$  signifies the dimension of the associated Hilbert space. Within this Hilbert space, the density operator is articulated in terms of basis states denoted as  $|i\rangle$ . Transitioning to Liouville space, the basis states are represented as  $|ij\rangle\rangle$ , effectively expanding the framework to accommodate the operator’s representation in this augmented space. These new basis states,  $|ij\rangle\rangle$ , form the foundation of Liouville space, in contrast to the basis states  $|i\rangle$ , which constitute the Hilbert space relevant to a spin system.

It is important to note that the conversion process of the density matrix from its representation in Hilbert space to Liouville space is independent of how the density operator is normalized. Consequently, this transformation technique is equally applicable to density operators normalized in terms of concentration.

### K. Matrix representations of observables in Liouville space

The *NMR signal* captured at a specified instance (*Signal*) is determined by computing the trace of the product between the observable  $\hat{O}$  and the concentration-normalized density operator  $\hat{\sigma}$ :

$$\text{Signal} = \text{Tr}(\hat{\sigma}\hat{O}) = \sum_{ij} \sigma_{ij} (O_{ij}^\dagger)^*. \quad (33)$$

Where  $O^\dagger$  is the conjugate transpose of the observable, and  $(O^\dagger)^*$  is the conjugate of the conjugate transpose.

Since  $\sigma_{ij} = \langle\langle ij|\sigma\rangle\rangle$  and  $(O_{ij}^\dagger)^* = \langle\langle O_{ij}^\dagger|ij\rangle\rangle$ , given  $|\sigma\rangle\rangle$  and  $(O^\dagger)\rangle\rangle$  mapped from  $\hat{\sigma}$  and  $\hat{O}^\dagger$  the measured signal can be calculate in Liouville space as

$$\begin{aligned} \text{Signal} &= \sum_{ij} \langle\langle O_{ij}^\dagger\rangle\rangle \langle\langle ij|\sigma\rangle\rangle \\ &= \langle\langle O^\dagger| \left( \sum_{ij} |ij\rangle\rangle \langle\langle ij| \right) |\sigma\rangle\rangle \\ &= \langle\langle O^\dagger|\sigma\rangle\rangle \end{aligned} \quad (34)$$

Here we use the fact that  $\sum_{ij} |ij\rangle\rangle \langle\langle ij|$  is equal to the identity superoperator ( $\hat{1}$ ).

The measured signal  $\langle\langle O^\dagger|\sigma\rangle\rangle$  is calculated by taking a matrix product between the column matrix  $|\sigma\rangle\rangle$  and the row-matrix  $\langle\langle O^\dagger|$ . Where the row-matrix can be expressed as:

$$\langle\langle O^\dagger| = |O^\dagger\rangle\rangle^\dagger = |O^T\rangle\rangle^T \quad (35)$$

### L. Matrix representations of linear transformations in Liouville space

In this section we prove the law of Linear Mapping by using a involving left multiplication by  $\hat{M}$  and a right multiplication by  $\hat{N}$

$$\begin{aligned} \hat{M} \cdot \hat{\rho} \cdot \hat{N} &= \sum_{ij} \rho_{ij} \hat{M}|i\rangle\langle j|\hat{N} \\ &= \sum_{ij} \rho_{ij} \left( \sum_k |k\rangle\langle k| \right) \hat{M}|i\rangle\langle j|\hat{N} \left( \sum_l |l\rangle\langle l| \right) \\ &= \sum_{ijkl} \rho_{ij} \langle k|\hat{M}|i\rangle\langle j|\hat{N}|l\rangle\langle k| \\ &= \sum_{ijkl} \rho_{ij} M_{ki} N_{jl} |k\rangle\langle l|. \end{aligned}$$

The transformed operator can be mapped into Liouville space with the substitution  $|k\rangle\langle l| = |kl\rangle$ . We deonte the mapped superoperator as  $|M\rho N\rangle\rangle$ .

$$\begin{aligned} |M\rho N\rangle\rangle &= \sum_{ijkl} \rho_{ij} M_{ki} N_{jl} |kl\rangle\rangle \quad \text{take } \rho_{ij} = \langle\langle ij|\rho\rangle\rangle, \\ |M\rho N\rangle\rangle &= \sum_{ijkl} \langle\langle ij|\rho\rangle\rangle M_{ki} N_{jl} |kl\rangle\rangle \\ &= \sum_{ijkl} M_{ki} N_{jl} |kl\rangle\rangle \langle\langle ij|\rho\rangle\rangle \\ &= \left( \sum_{ijkl} M_{ki} N_{jl} |k\rangle\langle i| \otimes |l\rangle\langle j| \right) |\rho\rangle\rangle \\ &= \left( \sum_{ijkl} M_{ki} N_{lj}^T |k\rangle\langle i| \otimes |l\rangle\langle j| \right) |\rho\rangle\rangle \\ &= \left( \sum_{ik} M_{ki} |k\rangle\langle i| \right) \otimes \left( \sum_{lj} N_{lj}^T |l\rangle\langle j| \right) |\rho\rangle\rangle \end{aligned}$$

$$\text{Since } \hat{M} = \sum_{ik} M_{ki} |k\rangle\langle i| \text{ and } \hat{N}^T = \sum_{lj} N_{lj}^T |l\rangle\langle j|,$$

$$|M\rho N\rangle\rangle = \hat{M} \otimes \hat{N}^T |\rho\rangle\rangle \quad (36)$$

$$\text{In summary } \hat{M} \cdot \hat{\rho} \cdot \hat{N} \Rightarrow \hat{M} \otimes \hat{N}^T |\rho\rangle\rangle$$

### M. Mathematics for Liouville-Von Neumann equation and Matrix representations Hamiltonian superoperators

First it is important to define the Liouville operator before going into the various matrix representations of Hamiltonians. This starts with understanding the Liouville-Von Neumann equation introduced in the introduction. Though we are referencing it within the form  $\frac{d}{dt}\hat{\rho}_i = \hat{L}_i\hat{\rho}_i$ , for this section we will break up the  $\hat{L}_i$  term, which was defined to be  $-i\hat{L}$ . Thus after inserting this into the previous expression the Liouville-Von Neumann equation can be written as such.

$$\frac{d}{dt}\hat{\rho} = -i\hat{L}\hat{\rho} = i[\hat{H}, \hat{\rho}] \quad (37)$$

(This is the Liouville equation commonly defined in textbooks [2]. When in this form, this is isomorphic to the Schrodinger equation which is

$$\frac{d}{dt}|\psi\rangle = -i\hat{H}|\psi\rangle. \quad (38)$$

Based on the isomorphism discussed in this textbook [2], we can define the Liouville operator as the following commutator.

$$\hat{L} = [\hat{H}, \cdot], \quad (39)$$

Thus specifically, when applying the Liouville operator to the density operator  $\hat{\rho}$ , within a Hilbert Space we get the following expression.

$$\hat{L}\hat{\rho} = [\hat{H}, \hat{\rho}] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H} \quad (40)$$

From this it can be seen that Hamiltonian acts on the density operator through the following commutator as seen from the form of the final expression.

Following that, the Hamiltonian superoperator, which as mentioned before, is simply just an extension of the concept of an operator, where a Hamiltonian operator maps one state to another state within a Hilbert space, a Hamiltonian superoperator simply just maps operators to operators, can be written as the following:

$$\hat{H} = \hat{H} \otimes \hat{1} - \hat{1} \otimes \hat{H}^T \quad (41)$$

This follows from the previously explained Law of Mapping (equation 36). Within this expression,  $\hat{1}$  represents the identity operator acting on the Hilbert space for that particular molecule.

#### *N. Manipulations of the LvN equation and Matrix representations of relaxation superoperators*

This section concerns itself with the mathematical representation of the Liouville–Von Neumann (LvN) equation, and thus will be more definition based rather than purely math based. The LvN equation was given previously in equation 37, which can be expanded on for the evolution of spin, which is governed by this representation of the LvN equation.

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i [\hat{H} + \hat{H}_1(t), \hat{\rho}(t)] \quad (42)$$

However, in order to combat the random fluctuating part of the Hamiltonian, an assumption (which is known as motional narrowing) is made. The assumption assumes that the correlation timescale of fluctuation ( $\tau$ ) is sufficiently short such that its product with the root-mean-square of the fluctuation is much less than a unity. In short the mathematical expression that is being assumed is  $\tau \cdot \delta H \ll 1$ .

This allows for the LvN equation to be written into this “master equation” of the density operator.

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}(t) = & -i[\hat{H}, \hat{\rho}(t)] \\ & - \frac{1}{2} \int_{-\infty}^{\infty} d\tau \left[ \hat{H}_1(t), \left[ e^{-i\hat{H}_0\tau} \hat{H}_1(t-\tau) e^{i\hat{H}_0\tau}, \hat{\rho}(t) \right] \right] \end{aligned} \quad (43)$$

Based on further simplifying assumptions with regards to the system, the time dependent Hamiltonian takes the following form,

$$\hat{H}_1(t) = - \sum_i \gamma_i \left( B_{ix}(t) \hat{I}_{ix} + B_{iy}(t) \hat{I}_{iy} + B_{iz}(t) \hat{I}_{iz} \right), \quad (44)$$

with  $B_{ix}$ ,  $B_{iy}$ , and  $B_{iz}$  representing random fluctuations on the  $i$ -th spin for their respective directions. When also assuming the fluctuations are independent, and also assuming the timescale of the fluctuation is much shorter than the timescale of coherent dynamics (this is known as extreme narrowing), we can further assume that the noise fields’ fluctuations are delta-correlated in time, which is given in the following expression.

$$\gamma_i^2 \overline{B_{i\alpha}(t) B_{j\beta}(t-\tau)} = \frac{1}{T_{1i}} \delta(\tau) \delta_{ij} \delta_{\alpha\beta} \quad (45)$$

Within this expression  $\frac{1}{T_{1i}}$  is the longitudinal relaxation time of the  $i$ -th spin, which a constant value that measured. Reinserting all of these simplifying expressions back into the LvN equation, we get the following expression.

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i [\hat{H}, \hat{\rho}(t)] - \hat{\hat{R}} \hat{\rho}(t), \quad (46)$$

Within this expression  $\hat{\hat{R}} \hat{\rho}(t)$  represents a collection of all the simplifying assumptions made, and is known as action of the relaxation superoperator and is defined as such.

$$\hat{\hat{R}} \hat{\rho}(t) = \sum_i \frac{1}{2T_{1i}} \sum_{\alpha=x,y,z} \left[ 2\hat{I}_{i\alpha} \hat{\rho}(t) \hat{I}_{i\alpha} - \hat{\rho}(t) \hat{I}_{i\alpha}^2 - \hat{I}_{i\alpha}^2 \hat{\rho}(t) \right] \quad (47)$$

Using the Law of Mapping (equation 36), within the Liouville space, we can rewrite this expression as,

$$\hat{\hat{R}} = \sum_i \frac{1}{2T_{1i}} \sum_{\alpha=x,y,z} \left[ 2\hat{I}_{i\alpha} \otimes \hat{I}_{i\alpha}^T - \hat{1} \otimes \hat{I}_{i\alpha}^2 - \hat{I}_{i\alpha}^2 \otimes \hat{1} \right] \quad (48)$$

Further, when assuming that the  $i$ -th spin has angular momentum quantum number  $L_i$ , that is assuming,  $\sum_{\alpha} \hat{I}_{i\alpha}^2 = L_i(L_i + 1) \hat{1}$ , we can simplify our prior expression as follows.

$$\hat{\hat{R}} = \sum_i \frac{1}{T_{1i}} \left[ \left( \sum_{\alpha=x,y,z} \hat{I}_{i\alpha} \otimes \hat{I}_{i\alpha}^T \right) - L_i(L_i + 1) \hat{1} \otimes \hat{1} \right] \quad (49)$$

Now when considering a system of only 1/2 spin particles (which is what we are concerned with), expression can finally be written as follows.

$$\hat{\hat{R}} = \sum_i \frac{1}{T_{1i}} \left( \sum_{\alpha=x,y,z} \hat{I}_{i\alpha} \otimes \hat{I}_{i\alpha}^T \right) - \frac{3}{4} \sum_i \frac{1}{T_{1i}} \hat{1} \otimes \hat{1} \quad (50)$$

Finally, in the context of this expression the individual spin relaxation time is stored within the matrix  $T_1$ . Specifically the matrix is given in the following form.  $T_1 = [T_{11} \ T_{12} \ ... T_{1N}]$ .

#### *O. Matrix representation of partial trace superoperators*

Starting with a simple example of dissociation to motivate the mathematical discussion, take the example where a molecule XY dissociates into X and Y, written as



with the density operator  $\hat{\rho}_{XY}$  being used to describe this dissociation. Now assume that the density operator  $\hat{\rho}_X$  takes the following form.

$$\hat{\rho}_X = \sum_{xx'} \rho_{xx'} |x\rangle \langle x'| \quad (52)$$

It should be noted that  $\rho_{xx'}$  is a constant and can be measured by taking a pseudo-measurement by taking the trace of the



observable  $|x'\rangle \langle x| \otimes \hat{1}_Y$ . This is given under the following expression.

$$\rho_{xx'} = \text{Tr} \left[ \left( |x'\rangle \langle x| \otimes \hat{1}_Y \right) \hat{\rho}_{XY} \right] \quad (53)$$

This expression can be further manipulated as the  $\hat{1}_Y$  operator can be expanded as

$$\hat{1}_Y = \sum_y |y\rangle \langle y|. \quad (54)$$

In this case,  $|y\rangle$  represents a basis state for molecule Y. Thus the part of expression inside the trace operator from equation 53 can be rewritten as

$$\begin{aligned} & |x'\rangle \langle x| \otimes \hat{1}_Y \\ &= \sum_y (|x'\rangle \otimes |y\rangle) (\langle x| \otimes \langle y|) = \sum_y |x'y\rangle \langle xy|. \end{aligned} \quad (55)$$

This result is based on the mixed-product property of the Kronecker product. Inserting equation 55 into the right side of equation 53, the final trace expression can be written as

$$\text{Tr} \left[ (|x'\rangle \langle x| \otimes \hat{1}_Y) \hat{\rho}_{XY} \right] = \sum_y \langle xy | \hat{\rho}_{XY} | x'y \rangle. \quad (56)$$

Finally, combining equation 56 and equation 53 and inserting this result into equation 52, the final density operator of x (written as  $\hat{\rho}_X$ ) can be written as

$$\begin{aligned} \hat{\rho}_X &= \sum_{xx'} |x\rangle \langle x'| \sum_y \langle xy | \hat{\rho}_{XY} | x'y \rangle \\ &= \sum_y \sum_{xx'} |x\rangle \langle x'| \langle xy | \hat{\rho}_{XY} | x'y \rangle \langle x'|. \end{aligned} \quad (57)$$

(keep in mind  $\rho_{xx'}$  is simply a scalar, which is why the order was switched for easier readability). Now by the following simplifications:

$$\begin{aligned} |x\rangle \langle xy| &= (|x\rangle \otimes 1)(\langle x| \otimes \langle y|) = (|x\rangle \langle x|) \otimes \langle y|, \\ |x'y\rangle \langle x'| &= (|x'\rangle \otimes |y\rangle)(\langle x'| \otimes 1) = (|x'\rangle \langle x'|) \otimes |y\rangle, \end{aligned} \quad (58)$$

From equations 58 and 57,  $\hat{\rho}_X$  can be written as

$$\begin{aligned} \hat{\rho}_X &= \sum_y \left[ \left( \sum_x |x\rangle \langle x| \right) \otimes \langle y| \right] \hat{\rho}_{XY} \left[ \left( \sum_{x'} |x'\rangle \langle x'| \right) \otimes |y\rangle \right] \\ &= \sum_y \left( \hat{1}_X \otimes \langle y| \right) \hat{\rho}_{XY} \left( \hat{1}_X \otimes |y\rangle \right). \end{aligned} \quad (59)$$

This gives us our final expression for  $\hat{\rho}_X$ . One can verify this result by testing it on the following density operator  $\hat{\rho}_X \otimes \hat{\rho}_Y$ . This yields the following results.

$$\begin{aligned} & \sum_y \left( \hat{1}_X \otimes \langle y| \right) \hat{\rho}_X \otimes \hat{\rho}_Y \left( \hat{1}_X \otimes |y\rangle \right) \\ &= \left( \hat{1}_X \hat{\rho}_X \hat{1}_X \right) \otimes \left( \sum_y \langle y | \hat{\rho}_Y | y \rangle \right) \\ &= \hat{\rho}_X \text{Tr}(\hat{\rho}_Y) = \hat{\rho}_X. \end{aligned} \quad (60)$$

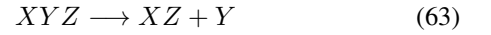
This is the expected result since  $\hat{\rho}_X$  is obtained by taking the partial trace over the degree of freedom of molecule Y. Thus based on this result, we can denote this entire transformation by the partial trace superoperator, which is defined as follows.

$$\hat{T}_Y^{(XY)} \hat{\rho}_{XY} = \sum_y \left( \hat{1}_X \otimes \langle y| \right) \hat{\rho}_{XY} \left( \hat{1}_X \otimes |y\rangle \right) \quad (61)$$

Written abstractly, within a Liouville space, it is known that this trace superoperator takes the following form based on the previously explained Mapping Law (equation 36), and the property that  $|y\rangle^T = \langle y|^*$ .

$$\hat{T}_Y^{(XY)} = \sum_y \left( \hat{1}_X \otimes \langle y| \right) \otimes \left( \hat{1}_X \otimes \langle y|^* \right). \quad (62)$$

As an application of this result, we will look at the case where molecule XYZ dissociates into XZ and Y, which is written as the following.



The density operator of molecule XY  $\hat{\rho}_{XY}$  is calculated by applying the partial trace superoperator  $\hat{T}_Y^{(XYZ)}$  to the density operator of  $\hat{\rho}_{XYZ}$ . This is given by the following expression.

$$\begin{aligned} \hat{\rho}_{XZ} &= \hat{T}_Y^{(XYZ)} \hat{\rho}_{XYZ} \\ &= \sum_y \left( \hat{1}_X \otimes \langle y| \otimes \hat{1}_Z \right) \hat{\rho}_{XYZ} \left( \hat{1}_X \otimes |y\rangle \otimes \hat{1}_Z \right) \end{aligned} \quad (64)$$

Within the above expression  $\{|Y\rangle\}$  represents a basis for molecule Y, and  $\hat{1}_X$  and  $\hat{1}_Y$  representing the identity operators of molecules X and Y respectively. Specifically for reactions of this form, the partial trace superoperator takes the form of the following.

$$\hat{T}_Y^{(XYZ)} = \sum_y \left( \hat{1}_X \otimes \langle y| \otimes \hat{1}_Z \right) \otimes \left( \hat{1}_X \otimes \langle y|^* \otimes \hat{1}_Z \right) \quad (65)$$

This is just a generalization of equation 62 from before to reactions of this form. Lastly for the practical calculations of the (which will be referenced in the Examples and Numerical Results), when equation 65 is represented in the defined Zeeman product basis, it is calculated as follows.

$$\begin{aligned} & \left( T_X^{(XYZ)} \right)_{ilnr,jkmpqs} = \\ & \sum_y (1_X)_{ij} (\langle y|)_k (1_Z)_{lm} (1_X)_{np} (\langle y|)_q (1_Z)_{rs} \\ &= \sum_y (1_X)_{ij} (1_Y)_{yk} (1_Z)_{lm} (1_X)_{np} (1_Y)_{yq} (1_Z)_{rs}. \end{aligned} \quad (66)$$

The code representation of this calculation is given as follows.

```
dX,dY,dZ = d_X,d_Y,d_Z #Input: the dimensions of molecule X, Y, and Z
IX,IY,IZ = np.eye(dX),np.eye(dY),np.eye(dZ)
Tr = np.einsum('ij,yk,lm,np,yq,rs->ilnr,jkmpqs',IX,IY,IZ,IX,IY,IZ).reshape((dX*dZ)**2,(dX*dY*dZ)**2)
```

### P. Matrix representations of Kronecker product superoperators

When considering the association of molecule X and molecule Y into molecule XY, the density operator of molecule XY ( $\hat{\rho}_{XY}$ ) can be expressed as the following Kronecker product:

$$\hat{\rho}_{XY} = \hat{\rho}_X \otimes \hat{\rho}_Y \quad (67)$$

This Kronecker product can be rewritten and expressed as the following,

$$\hat{\rho}_X \otimes \hat{\rho}_Y = \sum_{yy'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) \hat{\rho}_X \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right) \quad (68)$$

where  $|y\rangle$  forms a basis of molecule Y and  $\hat{\mathbf{1}}_X$  represents the identity operator acting on the Hilbert Space of molecule X.

This is proven by expanding the  $\hat{\rho}_X$  term since  $\hat{\rho}_X = \sum_{xx'} \rho_{xx'} |x\rangle \langle x'|$ , we can expand the prior equation as follows.

$$\begin{aligned} & \sum_{yy'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) \hat{\rho}_X \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right) \\ &= \sum_{xx'} \rho_{xx'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) |x\rangle \langle x'| \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right). \end{aligned} \quad (69)$$

Following this, since  $|x\rangle \langle x'| = (|x\rangle \langle x'|) \otimes 1$ , we use the mixed-product property to simplify as follows.

$$\begin{aligned} & \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) |x\rangle \langle x'| \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right) \\ &= \left( \hat{\mathbf{1}}_X |x\rangle \langle x'| \hat{\mathbf{1}}_X \right) \otimes (|y\rangle \langle y'|) \\ &= |x\rangle \langle x'| \otimes |y\rangle \langle y'|. \end{aligned} \quad (70)$$

Now inserting these results back into the summation, we are left with the complete proof for the expression.

$$\begin{aligned} & \sum_{xx'yy'} \rho_{xx'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) |x\rangle \langle x'| \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right) \\ &= \sum_{xx'yy'} \rho_{xx'} \rho_{yy'} |x\rangle \langle x'| \otimes |y\rangle \langle y'| \\ &= \left( \sum_{xx'} \rho_{xx'} |x\rangle \langle x'| \right) \otimes \left( \sum_{yy'} \rho_{yy'} |y\rangle \langle y'| \right) \\ &= \hat{\rho}_X \otimes \hat{\rho}_Y, \end{aligned} \quad (71)$$

Based on this result, it can be seen that the Kronecker product can be viewed as a result of a linear transformation acting upon  $\hat{\rho}_X$ . This linear transformation will be defined as Kronecker product superoperator as follows.

$$\hat{\hat{D}}_Y^{(XY)} \hat{\rho}_X = \sum_{yy'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) \hat{\rho}_X \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right) \quad (72)$$

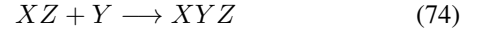
where  $\hat{\hat{D}}_Y^{(XY)}$  is defined as the Kronecker product superoperator. Written more abstractly, in a Liouville space, the

Kronecker product superoperator is represented simply by the following expression.

$$\hat{\hat{D}}_Y^{(XY)} = \sum_{yy'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \right) \otimes \left( \hat{\mathbf{1}}_X \otimes \langle y'| \right)^* \quad (73)$$

This was a result of simply applying the Law of Mapping (equation 36), where  $|y'\rangle^* = \langle y'|^T$ .

As an application of this result, we will look at the case where molecule XZ associates with Y to form molecule XYZ, which are given under the following form.



The density operator of molecule XYZ  $\hat{\rho}_{XYZ}$  is calculated by applying the Kronecker product superoperator  $\hat{\hat{D}}_Y^{(XYZ)}$  to the density operator of  $\hat{\rho}_{XZ}$ . This is written as follows.

$$\hat{\rho}_{XYZ} = \hat{\hat{D}}_Y^{(XYZ)} \hat{\rho}_{XZ} \quad (75)$$

Where the Kronecker product superoperator  $\hat{\hat{D}}_Y^{(XYZ)}$  to the density operator of  $\hat{\rho}_{XZ}$  is given by the following expression for reactions of this form.

$$\hat{\hat{D}}_Y^{(XYZ)} = \sum_{yy'} \rho_{yy'} \left( \hat{\mathbf{1}}_X \otimes |y\rangle \otimes \hat{\mathbf{1}}_Z \right) \otimes \left( \hat{\mathbf{1}}_X \otimes |y'\rangle^* \otimes \hat{\mathbf{1}}_Z \right) \quad (76)$$

This is simply just a generalization of equation 73 for reactions of this form. Represented in the defined Zeeman product basis, the Kronecker product superoperator is calculated as follows.

$$\begin{aligned} & \left( \hat{D}_Y^{(XYZ)} \right)_{iklnqr,jmps} = \\ & \sum_{y,y'} (\mathbf{1}_X)_{ij} (|y\rangle)_k (\mathbf{1}_Z)_{lm} (\mathbf{1}_X)_{np} (|y'\rangle)_q (\mathbf{1}_Z)_{rs} \rho_{yy'} \\ &= \sum_{y,y'} (\mathbf{1}_X)_{ij} (\mathbf{1}_Y)_{ky} (\mathbf{1}_Z)_{lm} (\mathbf{1}_X)_{np} (\mathbf{1}_Y)_{qy'} (\mathbf{1}_Z)_{rs} \rho_{yy'}. \end{aligned} \quad (77)$$

This is calculated in code as follows.

```
#Input: The dimensions of molecule X, Y and Z;
# The density matrix of molecule Y.
dY,dY,dZ,rho = d_X,d_Y,d_Z,rho_Y
IX,IY,IZ = np.eye(dX),np.eye(dY),np.eye(dZ)
Kron = np.einsum('ij,ky,lm,np,ql,rs,yf->iklnqr,jmps',IX,IY,IZ,IX,IY,IZ,rho).reshape((dX*dY*dZ)**2,(dX*dZ)**2)
```

### Q. Derivation of the Time-Dependent Spin Equation

We begin our derivation using the assumptions discussed in the introduction

- 1) Individual events of association and dissociation occurs much faster than nuclear spin dynamics
- 2) The state of molecule B remains unchanged
- 3) Chemical kinetic rates are independent of the nuclear spin degrees of freedom.

We begin by analyzing the association and dissociation process at the single molecule level using a density operator approach.

We let  $\hat{\rho}_A$  and  $\hat{\rho}_B$  denote the density operators of arbitrary molecules A and B respectively immediately prior to their association. The density operator of the associated molecule AB is obtained by taking the Kronecker product between  $\hat{\rho}_A$  and  $\hat{\rho}_B$ . We express this product in a form that is linearly dependent on  $\hat{\rho}_A$  as:

$$\hat{\rho}_A \otimes \hat{\rho}_B = \hat{D}_B^{(AB)} \hat{\rho}_A \quad (78)$$

The association superoperator  $\hat{D}_B^{(AB)}$  acts on  $\hat{\rho}_B$  and transforms it into  $\hat{\rho}_A \otimes \hat{\rho}_B$ . The superscript AB indicates the order in which the Kronecker product takes place.

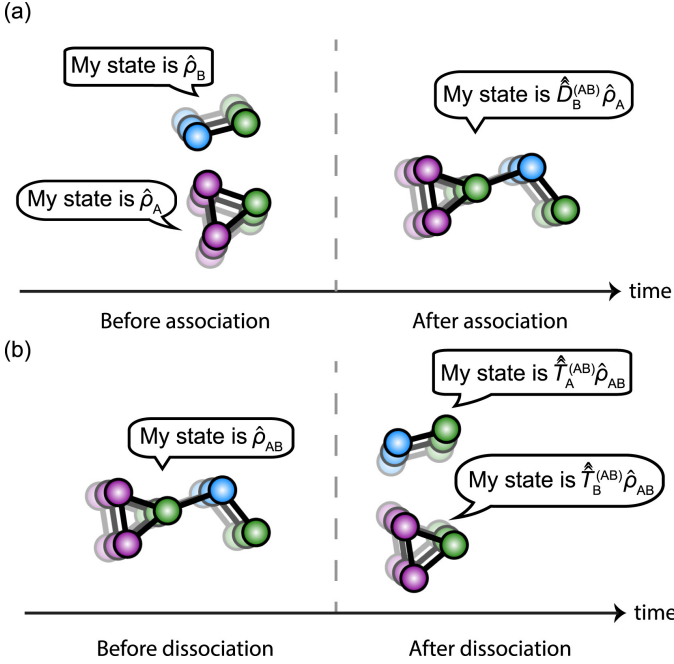


Fig. 3. Spin states of individual molecules A, B, and AB before and after (a) the association event and (b) the dissociation event.

A similar approach applies to the dissociation process illustrated above where molecule AB dissociates into molecules A and B. We let  $\hat{\rho}_{AB}$  denote the density operator of molecule AB at the moment prior to dissociation. The density operator of dissociated molecule is the partial trace on  $\hat{\rho}_{AB}$  over the degrees of freedom associated with molecule B, resulting in  $\text{Tr}_B(\hat{\rho})_{AB}$ . This partial trace is expressed in linearly dependent form on  $\hat{\rho}_{AB}$  as

$$\text{Tr}_B(\hat{\rho}_{AB}) = \hat{T}_B^{AB} \hat{\rho}_{AB} \quad (79)$$

We now examine the effect of chemical exchange on the density operator on an ensemble level temporarily disregarding the effects of coherent evolution and incoherent relaxation. Let  $\hat{\rho}_A$  and  $\hat{\rho}_{AB}$  represent the ensemble-averaged density operators for molecules A and AB. After a short time interval  $\Delta t$  these density operators evolve due to chemical exchange. The

evolved density operators are obtained by taking a weighted-average between the ensembles of non-reacted molecules and those generated  $\Delta t$ .

Assuming that  $\Delta t$  is small enough such that each individual molecule reacts at most once, we can determine the concentrations and density operators of the non-reacted and reaction-produced molecules for A and AB after  $\Delta t$ . Let  $n_a$  and  $n_d$  denote the concentrations of molecules A and AB consumed during  $\Delta t$ , respectively. For molecule A, the concentrations of non-reacted and reaction-produced A molecules are  $[A] - n_a$  and  $n_d$ , respectively, while their density operators are  $\hat{\rho}_A$  and  $\hat{T}_B^{(AB)} \hat{\rho}_{AB}$ .

Similarly, for AB, the concentrations of non-reacted and reaction-produced molecules are  $[AB] - n_d$  and  $n_a$ , respectively, and their density operators are  $\hat{\rho}_{AB}$  and  $\hat{D}_B^{(AB)} \hat{\rho}_A$ .

Consequently, the evolved density operators for molecules A and AB are determined by taking the concentration-weighted averages of the density operators of the non-reacted and the reaction-produced molecules, as discussed earlier. Let  $\Delta \hat{\rho}_A$  and  $\Delta \hat{\rho}_{AB}$  represent the changes of the density operators for molecules A and AB, respectively, during the time interval  $\Delta t$ . The evolved density operators are expressed as:

$$\hat{\rho}_A + \Delta \hat{\rho}_A = \frac{([A] - n_a) \hat{\rho}_A + n_d \hat{T}_B^{(AB)} \hat{\rho}_{AB}}{[A] - n_a + n_d} \quad (80)$$

$$\hat{\rho}_{AB} + \Delta \hat{\rho}_{AB} = \frac{([AB] - n_d) \hat{\rho}_{AB} + n_a \hat{D}_B^{(AB)} \hat{\rho}_A}{[AB] - n_d + n_a} \quad (81)$$

Let  $\Delta[A]$  and  $\Delta[AB]$  denote the concentration changes for molecules A and AB, respectively, during the time interval  $\Delta t$ . Since  $\Delta[A] = -n_a + n_d$  and  $\Delta[AB] = n_a - n_d$ , we can substitute  $-n_a + n_d$  with  $\Delta[A]$  and  $n_a - n_d$  with  $\Delta[AB]$  in the denominators. By multiplying both sides of the equations by the corresponding denominators, we can rearrange the equations as follows:

$$([A] + \Delta[A])(\hat{\rho}_A + \Delta \hat{\rho}_A) - [A] \hat{\rho}_A = -n_a \hat{\rho}_A + n_d \hat{T}_B^{(AB)} \hat{\rho}_{AB} \quad (82)$$

$$([AB] + \Delta[AB])(\hat{\rho}_{AB} + \Delta \hat{\rho}_{AB}) - [AB] \hat{\rho}_{AB} = -n_d \hat{\rho}_{AB} + n_a \hat{D}_B^{(AB)} \hat{\rho}_A \quad (83)$$

Since the left sides of the equations above can be further simplified as

$$([A] + \Delta[A])(\hat{\rho}_A + \Delta \hat{\rho}_A) - [A] \hat{\rho}_A = \Delta(\hat{\rho}_A);$$

$$([AB] + \Delta[AB])(\hat{\rho}_{AB} + \Delta \hat{\rho}_{AB}) - [AB] \hat{\rho}_{AB} = \Delta(\hat{\rho}_{AB}). \quad (84)$$

We introduce the concentration-normalized density operators  $\hat{\sigma}_A = [A]\hat{\rho}_A$  and  $\hat{\sigma}_{AB} = [AB]\hat{\rho}_{AB}$  for molecules A and AB, respectively. Indeed, the use of concentration-normalized density operators is particularly beneficial when discussing the equations of motion for systems undergoing non-equilibrium chemical reactions. In these systems, the concentrations of participating molecules are time-dependent. The changes of the concentration-normalized density operators during the time interval  $\Delta t$  are readily obtained as:

$$\Delta(\hat{\sigma}_A) = -n_a\hat{\rho}_A + n_d\hat{T}_B^{(AB)}\hat{\rho}_{AB} \quad (85)$$

$$\Delta(\hat{\sigma}_{AB}) = -n_d\hat{\rho}_{AB} + n_a\hat{D}_B^{(AB)}\hat{\rho}_A. \quad (86)$$

Based on Eq. (1), we insert  $n_a = \tilde{k}_a[A]\Delta t$  and  $n_d = k_d[AB]\Delta t$ , and divide both sides of the equations by  $\Delta t$ :

$$\frac{\Delta\hat{\sigma}_A}{\Delta t} = -\tilde{k}_a\hat{\sigma}_A + k_d\hat{T}_B^{(AB)}\hat{\sigma}_{AB}; \quad (87)$$

$$\frac{\Delta\hat{\sigma}_{AB}}{\Delta t} = \tilde{k}_a\hat{D}_B^{(AB)}\hat{\sigma}_A - k_d\hat{\sigma}_{AB}. \quad (88)$$

In the limit  $\Delta t \rightarrow 0$ , we derive the evolution of the concentration-normalized density operators solely due to chemical exchange:

$$\frac{d}{dt}\hat{\sigma}_A = -\tilde{k}_a\hat{\sigma}_A + k_d\hat{T}_B^{(AB)}\hat{\sigma}_{AB} \quad (89)$$

$$\frac{d}{dt}\hat{\sigma}_{AB} = +\tilde{k}_a\hat{D}_B^{(AB)}\hat{\sigma}_A - k_d\hat{\sigma}_{AB} \quad (90)$$

Similarly to Eq. (1), we can write the equations in matrix form as

$$\frac{d}{dt} \begin{pmatrix} \hat{\sigma}_A \\ \hat{\sigma}_{AB} \end{pmatrix} = \begin{pmatrix} -\tilde{k}_a\hat{1}_A & k_d\hat{T}_B^{(AB)} \\ k_a\hat{D}_B^{(AB)} & -k_d\hat{1}_{AB} \end{pmatrix} \begin{pmatrix} \hat{\sigma}_A \\ \hat{\sigma}_{AB} \end{pmatrix}. \quad (91)$$

Here  $\hat{1}_A$  and  $\hat{1}_{AB}$  are identity superoperators that act on  $\hat{\sigma}_A$  and  $\hat{\sigma}_{AB}$ , respectively and  $\hat{1}_A$  and  $\hat{1}_{AB}$  are identity superoperators matrices for the corresponding species.

In terms of the effects of coherent evolution and incoherent relaxation, the evolution of the concentration-normalized density operator in the absence of chemical exchange follows the same form as described in Eq. (2). This is because Eq. (2) is unaffected by the specific normalization used. Building on Eq. (2), we can express the evolution of the concentration-normalized density operators for molecules A and C in matrix form as follows:

$$\frac{d}{dt} \begin{pmatrix} \hat{\sigma}_A \\ \hat{\sigma}_C \end{pmatrix} = \begin{pmatrix} \hat{L}_A & 0 \\ 0 & \hat{L}_C \end{pmatrix} \begin{pmatrix} \hat{\sigma}_A \\ \hat{\sigma}_C \end{pmatrix}. \quad (92)$$

We can now combine the effects of chemical exchange, coherent evolution, and incoherent relaxation by summing their respective coefficient matrices. This enables us to express the evolution of the concentration-normalized density operators in a matrix form as follows:

$$\frac{d}{dt} \begin{pmatrix} \hat{\sigma}_A \\ \hat{\sigma}_C \end{pmatrix} = \left( \begin{pmatrix} \hat{L}_A & 0 \\ 0 & \hat{L}_C \end{pmatrix} + \begin{pmatrix} -k_a\hat{1}_A & k_d^{(AB)}\hat{1}_B \\ k_a^{(AB)}\hat{1}_B & -k_d\hat{1}_C \end{pmatrix} \right) \begin{pmatrix} \hat{\sigma}_A \\ \hat{\sigma}_C \end{pmatrix}. \quad (93)$$

### R. Special cases: Solving the Steady State

It should be noted that there are some cases where the steady state of the system suffices. Thus instead of solving the evolution of the system as will be discussed later in the Examples and Numerical Results section, one may solve for the simpler Steady State case. To solve the steady state of the system, one must find the null-space (or kernel) of M, the coefficient matrix. This is done by simply finding the eigenvector corresponding to an eigenvalue of zero.

```
sigma = null_space(M)
rho_A = np.reshape(sigma[d_A**2], (d_A, d_A), order='F')
rho_A = rho_A/np.trace(rho_A)
rho_AB = np.reshape(sigma[d_A**2:d_A**2+d_AB**2], (d_AB, d_AB), order='F')
rho_AB = rho_AB/np.trace(rho_AB)
```

Fig. 4. Code to obtain the steady state solution (finding the null-space)

This is demonstrated with the code above, where the function "null\_space" is from the NumPy library and simply computes the null space of the given parameter matrix.

## V. EXAMPLES AND NUMERICAL RESULTS:

### A. Step 1: Specify the spin systems

For our Examples section we will conceptually run through the equations one would use for calculating the zero-field NMR spectra of  $\text{NH}_3$  and  $\text{NH}_4^+$  molecules undergoing chemical exchange. This process, builds ideas of what is going on though the code developed from the paper located in the appendix A. The program was developed in Python, but in theory could be built in any matrix solving utility using the following generalized steps.

For this example using the  $\text{NH}_3$  and  $\text{NH}_4^+$  molecules undergoing chemical exchange.  $\text{NH}_3$  have a spin system of 4, indicating a system of 4  $\frac{1}{2}$ -spin protons forming the molecule. Where  $\text{NH}_4^+$  has a 5 spin system.

### B. Step 2: Construct the Hamiltonian super operator

To begin we must construct the Hamiltonian itself. To start we are using the single spin  $\frac{1}{2}$  nuclei angular momentum operators given in a Zeeman basis

$$\begin{aligned} \hat{I}_x &= \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ \hat{I}_y &= \frac{1}{2i} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \\ \hat{I}_z &= \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{aligned} \quad (94)$$

To transform these into the multi nuclei molecule angular momentum operators we can use the following equation the we developed earlier in 29.

$$\hat{I}_{i\alpha} = 1_{i-1} \otimes \hat{I}_\alpha \otimes 1_{n-1} \quad (95)$$

For the,  $\text{NH}_3$  4 spin system we calculate all the momentum operators up to  $i = 4$ . And, for ease of calculation we store these in a 4d matrix S:

$$S_{\text{NH3}} = \begin{bmatrix} \hat{I}_{1x} & \hat{I}_{1y} & \hat{I}_{1z} \\ \hat{I}_{2x} & \hat{I}_{2y} & \hat{I}_{2z} \\ \hat{I}_{3x} & \hat{I}_{3y} & \hat{I}_{3z} \\ \hat{I}_{4x} & \hat{I}_{4y} & \hat{I}_{4z} \end{bmatrix} \quad (96)$$

For the  $\text{NH}_4^+$  5 spin system we do the same but up to  $i = 5$

$$S_{\text{NH4}} = \begin{bmatrix} \hat{I}_{1x} & \hat{I}_{1y} & \hat{I}_{1z} \\ \hat{I}_{2x} & \hat{I}_{2y} & \hat{I}_{2z} \\ \hat{I}_{3x} & \hat{I}_{3y} & \hat{I}_{3z} \\ \hat{I}_{4x} & \hat{I}_{4y} & \hat{I}_{4z} \\ \hat{I}_{5x} & \hat{I}_{5y} & \hat{I}_{5z} \end{bmatrix} \quad (97)$$

For convenience, we store the J-couplings,  $J_{ij}$ , in matrix form as follows:

$$J_0 = \begin{bmatrix} 0 & J_{12} & \cdots & J_{1n} \\ 0 & 0 & \cdots & J_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 0 \end{bmatrix} \quad (98)$$

Where  $J_{ij}$  represents the J-coupling scalar spin-spin terms between i-th and j-th spins.

So with this form along with known J-coupling terms provided by the paper we can construct these matrices for each of the molecules in (Hz)

$$J_{\text{NH3}} = \begin{bmatrix} 0 & -73.4 & -73.4 & -73.4 \\ 0 & 0 & -16.9 & -16.9 \\ 0 & 0 & 0 & -16.9 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (99)$$

$$J_{\text{NH4}} = \begin{bmatrix} 0 & -73.4 & -73.4 & -73.4 & -73.4 \\ 0 & 0 & -16.9 & -16.9 & -16.9 \\ 0 & 0 & 0 & -16.9 & -16.9 \\ 0 & 0 & 0 & 0 & -16.9 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (100)$$

Now to construct the Hamiltonian we use the equation shown in (29) but using our created S matrix along with The  $J_0$  matrices defined above

First for  $\text{NH}_3$  take  $S = S_{\text{NH3}}$  and  $J = J_{\text{NH3}}$

$$\hat{H}_{\text{NH3}} = \sum_{i=1}^3 \sum_{j=i+1}^3 J_{ij} \left( \sum_{\alpha=1}^3 S_{i\alpha} S_{j\alpha} \right) \quad (101)$$

Similarly for  $\text{NH}_4$  take  $S = S_{\text{NH4}}$  and  $J = J_{\text{NH4}}$

$$\hat{H}_{\text{NH4}} = \sum_{i=1}^4 \sum_{j=i+1}^4 J_{ij} \left( \sum_{\alpha=1}^3 S_{i\alpha} S_{j\alpha} \right) \quad (102)$$

Because of the large of the matrices its impractical to show values moving forward.

The Super-operator follows is built as follows. Where  $\hat{1}_k$  is built like previously as a  $2^k \times 2^k$  identity matrix.

$$\hat{H}_{\text{NH3}} = \hat{H}_{\text{NH3}} \otimes \hat{1}_4 - \hat{1}_4 \otimes \hat{H}_{\text{NH3}}^T \quad (103)$$

$$\hat{H}_{\text{NH4}} = \hat{H}_{\text{NH4}} \otimes \hat{1}_5 - \hat{1}_5 \otimes \hat{H}_{\text{NH4}}^T \quad (104)$$

### C. Step 3: Construct the relaxation super operator

First we can define the longitudinal relaxation time of each i spin. For convenience we can store these constants in a vector corresponding to  $\text{NH}_3$  and  $\text{NH}_4$ . These again are known values that our paper provides for us.

$$T_{\text{NH3}} = [5 \quad 1 \quad 1 \quad 1] \quad (105)$$

$$T_{\text{NH4}} = [5 \quad 1 \quad 1 \quad 1 \quad 1] \quad (106)$$

With this and the previously defined Identity operator  $\hat{1}_k$  and angular momentum operator matrices  $S_{\text{NH3}}$  and  $S_{\text{NH4}}$  we can now construct the relaxation superoperators using equation derived in IV-N. Note  $\hat{1}_k \otimes \hat{1}_k = \hat{1}_{2k}$

for  $\text{NH}_3$  Take  $S = S_{\text{NH3}}$ :

$$\hat{R} = \sum_i^4 \frac{1}{T_{1i}} \left( \sum_{\alpha=1}^3 S_{i\alpha} \otimes S_{i\alpha}^T \right) - \frac{3}{4} \sum_i^4 \frac{1}{T_{1i}} \hat{1}_8 \quad (107)$$

for  $\text{NH}_4$  Take  $S = S_{\text{NH4}}$ :

$$\hat{R} = \sum_i^5 \frac{1}{T_{1i}} \left( \sum_{\alpha=1}^3 S_{i\alpha} \otimes S_{i\alpha}^T \right) - \frac{3}{4} \sum_i^5 \frac{1}{T_{1i}} \hat{1}_{10} \quad (108)$$

### D. Step 4: Construct the chemical exchange super operator

For later calculation will we need partial trace superoperators and the Kronecker product superoperators for this system. This will characterize for the dynamics of the exchange between  $\text{NH}_3$  and  $\text{NH}_4$

1) *partial trace superoperators*: We can first denote our ammonia molecules as a product of 4 protons as follows:  $[\text{NH}_4\text{H}_3\text{H}_2\text{H}_1]^+$ . Each of these protons has an equal chance of dissociation so to obtain the total partial trace super operator we must find the individual partial trace superoperators. Combing them at the end to generate the overall operator.

First we will look into the dissociation of the  $\text{H}_A$  proton notated as:



This becomes an example of the case:  $\text{XYZ} \rightarrow \text{XY} + \text{Z}$  in IV-O Where  $\text{X} = \text{N}$ ,  $\text{Y} = \text{H}_A$ , and  $\text{Z} = \text{H}_3\text{H}_2\text{H}_1$ . So using the derived equation we can calculate the partial trace superoperators using  $\langle y | = [1 \quad 0]$  for this case. Shown as

$$T_4 = \hat{1}_1 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_3 \otimes \hat{1}_1 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_3 \\ + \hat{1}_1 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_3 \otimes \hat{1}_1 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_3 \quad (110)$$

In the case of the dissociation of the  $H_B$  written as

$$[^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \rightarrow [^{15}\text{NH}_A\text{H}_C\text{H}_D] + \text{H}_B^+ \quad (111)$$

In this case  $X = ^{15}\text{NH}_A$ ,  $Y = \text{H}_B$ , and  $Z = \text{H}_C\text{H}_D$ . Where instead the dimension of there corresponding Hilbert spaces will be 4, 2, 4.

Using similar assumptions as before the form will be represented as  $T_3$

$$T_3 = \hat{1}_2 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_2 \otimes \hat{1}_2 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_2 \\ + \hat{1}_2 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_2 \otimes \hat{1}_2 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_2 \quad (112)$$

Next looking at the dissociation of  $H_C$  with the form

$$[^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \rightarrow [^{15}\text{NH}_A\text{H}_B\text{H}_D] + \text{H}_C^+ \quad (113)$$

Where  $X = ^{15}\text{NH}_A\text{H}_B$  with Hilbert space dimension 8,  $Y = \text{H}_C$  with Hilbert space dimension 2, and  $Z = \text{H}_D$  with Hilbert space dimension 2.

Using similar assumptions as before the form will be represented as  $T_2$

$$T_2 = \hat{1}_3 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_1 \otimes \hat{1}_3 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_1 \\ + \hat{1}_3 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_1 \otimes \hat{1}_3 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_1 \quad (114)$$

Finally, looking at the dissociation  $H_D$  with the form

$$[^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \rightarrow [^{15}\text{NH}_A\text{H}_B\text{H}_C] + \text{H}_D^+ \quad (115)$$

This will instead follow the first example case from IV-O where  $X = ^{15}\text{NH}_A\text{H}_B\text{H}_C$  with Hilbert space dimension 16, and  $Y = \text{H}_D$  with Hilbert space dimension 2. Using similar assumptions as before the form will be represented as  $T_1$

$$T_1 = \hat{1}_4 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \otimes \hat{1}_4 \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \\ + \hat{1}_4 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \hat{1}_4 \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (116)$$

We can then combine the previous superoperators, into an overall Partial Trace Super Operator for the entire chemical exchange, by taking an average. This evaluates to the following:

$$T = \frac{1}{4} (T_1 + T_2 + T_3 + T_4) \quad (117)$$

2) *Kronecker product superoperators*: We now instead look at protons being added to the molecule denoted as follows:

$H_C$  with the form

$$[^{15}\text{NH}_B\text{H}_C\text{H}_D] + \text{H}_A^+ \rightarrow [^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \quad (118)$$

This is the same as for the example case of IV-P where  $X = ^{15}\text{N}$ ,  $Y = \text{H}_A$ , and  $Z = \text{H}_B\text{H}_C\text{H}_D$ . First we construct a density matrix for molecule our reaction through the following form.

$$\rho_Y = \begin{bmatrix} \rho_{\alpha\alpha} & \rho_{\alpha\beta} \\ \rho_{\beta\alpha} & \rho_{\beta\beta} \end{bmatrix} \quad (119)$$

In our case for the exchange between  $\text{NH}_3$  and  $\text{NH}_4$  we can define  $\rho$  as follows:

$$\rho_Y = \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{bmatrix} \quad (120)$$

Which using the density matrix and equation derived in IV-P. This allows us to calculate the Kronecker product super operator for the association of  $\text{H}_A$  to the molecule as follows:

$$\text{Kron}_1 = \frac{1}{2} \hat{1}_1 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_3 \otimes \hat{1}_1 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_3 \\ + \frac{1}{2} \hat{1}_1 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_3 \otimes \hat{1}_1 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_3 \quad (121)$$

Next we can look at the association of  $\text{H}_B$  written as

$$[^{15}\text{NH}_A\text{H}_C\text{H}_D] + \text{H}_B^+ \rightarrow [^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \quad (122)$$

We define the particles as  $X = ^{15}\text{NH}_A$ ,  $Y = \text{H}_B$ , and  $Z = \text{H}_C\text{H}_D$ . We can calculate the super operator as follows:

$$\text{Kron}_2 = \frac{1}{2} \hat{1}_1 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_2 \otimes \hat{1}_2 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_2 \\ + \frac{1}{2} \hat{1}_2 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_2 \otimes \hat{1}_1 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_2 \quad (123)$$

If the associated particles is  $\text{H}_C$  it can be described as

$$[^{15}\text{NH}_A\text{H}_B\text{H}_D] + \text{H}_C^+ \rightarrow [^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \quad (124)$$

We can take  $X = ^{15}\text{NH}_A\text{H}_B$ ,  $Y = \text{H}_C$ , and  $Z = \text{H}_D$  Which allows us to define the super operator as follows

$$\text{Kron}_3 = \frac{1}{2} \hat{1}_3 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_1 \otimes \hat{1}_3 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_1 \\ + \frac{1}{2} \hat{1}_3 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_1 \otimes \hat{1}_3 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_1 \quad (125)$$

And finally we look at the association of  $\text{H}_B$  described as

$$[^{15}\text{NH}_A\text{H}_B\text{H}_C] + \text{H}_D^+ \rightarrow [^{15}\text{NH}_A\text{H}_B\text{H}_C\text{H}_D] \quad (126)$$



We can take  $X = {}^{15}\text{NH}_4\text{H}_8\text{H}_8\text{C}$ ,  $Y = \text{H}_2$ . Which allows us to form the Kronecker super operator as follows:

$$\begin{aligned} \text{Kron}_4 = & \frac{1}{2} \hat{1}_3 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_4 \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \hat{1}_1 \\ & + \frac{1}{2} \hat{1}_4 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_4 \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \hat{1}_4 \end{aligned} \quad (127)$$

We can then combine the previous Super operators to an overall Kronecker product Super Operator as follows

$$\text{Kron} = \frac{1}{4} (\text{Kron}_1 + \text{Kron}_2 + \text{Kron}_3 + \text{Kron}_4) \quad (128)$$

#### E. Step 5: Construct the coefficient matrix for the composite system

Within this section, we will go over the matrix representations of previously introduced concepts and tie everything up. As a precursor to all of this, from now on, whenever we reference  $A$ , we are referring to  $\text{NH}_3$  and whenever we reference  $B$  we are referring to  $\text{H}^+$  and  $AB$  represents  $\text{NH}_4^+$  for the purposes of this entire section as an example. First and foremost, we will write the previously introduced coefficient matrix (from section Q equation 93),

$$\begin{pmatrix} L_A - k_a 1_{2A} & k_d T_b^{(AB)} \\ k_a D_b^{(AB)} & L_{AB} - k_d 1_{2AB} \end{pmatrix} \quad (129)$$

Within this matrix,  $1_A$  and  $1_{2AB}$  are matrices that represent the identity superoperators  $\hat{1}_A$  and  $\hat{1}_{AB}$  respectively. Similarly,  $L_A$  and  $L_{AB}$  are the matrix representations of the Liouvillians for molecule A and molecule AB respectively. Specifically, the calculation for  $L_A$  and  $L_{AB}$  are given below.

$$L_A = -iH_A + R_A$$

$$L_{AB} = -iH_{AB} + R_{AB}$$

In this code,  $H_A$  and  $H_{AB}$  represent the matrix forms of the Hamiltonian superoperators for molecules A and AB that were explained in section M, while  $R_A$  and  $R_{AB}$  represent the matrix forms of the relaxation superoperators for molecules A and AB, as was defined in section N. Following that we use this code to calculate the M coefficient matrix from the introduction.

```
M = np.block([[L_A - ka*np.eye(d_A**2), kd*Tr],
               [ka*Kron, L_AB - kd*np.eye(d_AB**2)]])
```

Fig. 5. Calculations of M coefficient matrix

In this code,  $\text{Tr}$  represents the matrix representation of the partial trace super operator explained in section O, while  $\text{Kron}$  represents the matrix representation of the Kronecker product super operator explained in section P.

#### F. Step 6: Construct the initial state vector for the composite system

Next we will determine the initial conditions, by determining the initial concentration-normalized density operators. This is calculated using the following code.

```
sigma_A = A*rho_A #A: the concentration of molecule A
sigma_AB = AB*rho_AB #AB: the concentration of molecule AB
```

Fig. 6. Calculations of concentration-normalized density operators

In this code,  $\rho_A$  and  $\rho_{AB}$  represent the initial density matrix for their corresponding molecules, and  $\sigma_A$  and  $\sigma_{AB}$  represent the density column for their respective molecules.

As a note, for our specific example, the initial density matrix for  $A = \text{NH}_3$  is represented as  $\gamma_{15} N I_{1z} + \gamma_{1H} (I_{2z} + I_{3z} + I_{4z} + I_{5z})$ , where as the initial density matrix for  $AB = \text{NH}_4^+$  is represented as  $\gamma_{15} N I_{1z} + \gamma_{1H} (I_{2z} + I_{3z} + I_{4z})$ . For the expression above  $\gamma$  represents the gyromagnetic ratio, which was defined in the introduction. Specifically  $\gamma_{15} N = -27.126 \times 10^6 T^{-1} s^{-1}$ , while  $\gamma_{1H} = 267.522 \times 10^6 T^{-1} s^{-1}$  [5].

Following this, we map these matrices into their corresponding density columns as explained in section J. Lastly, the entire system's initial density column (which is denoted as  $\text{sigma}_0$ ) is given by concatenating the two calculated density columns.

The following figure provides a good summary of the dimensions of the various matrices involved in the LvN equation.

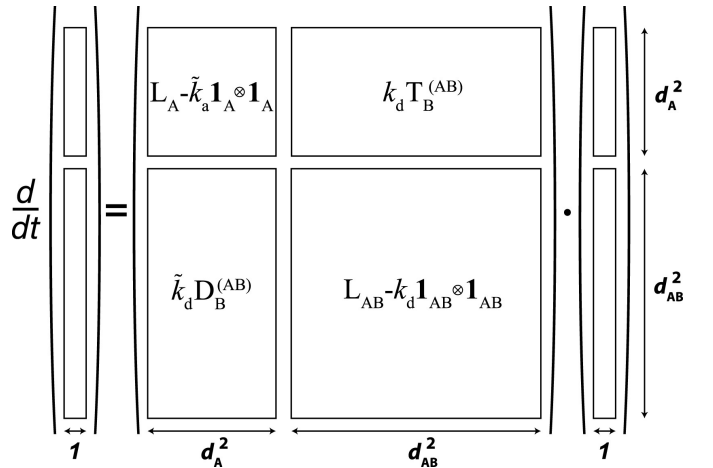


Fig. 7. Matrix Representation of the LvN equation

#### G. Step 7: Solving the System's State Vector

In order to evolution of the entire system in the one must first develop the theory to solve the matrix differential equation shown in the prior figure. The column vector  $\text{sigma}_0$  represents the initial conditions for this differential equation. This differential equation is solved by defining a sequence of

points from the start time to the end time with a time step of  $\Delta t$ . Using this method, the state vector of the system is consistently updated using the following expression.

$$\begin{pmatrix} |\sigma_A(t + \Delta t)\rangle \\ |\sigma_{AB}(t + \Delta t)\rangle \end{pmatrix} = \exp(M\Delta t) \begin{pmatrix} |\sigma_A(t)\rangle \\ |\sigma_{AB}(t)\rangle \end{pmatrix} \quad (130)$$

To clarify, within this expression,  $\exp$  represents the matrix exponential as  $M\Delta t$  is a matrix. The following is the code representation for the discussed equation.

```
Uevol = expm(M*dt)
sigma = np.matmul(Uevol, sigma)
```

Fig. 8. Code representation for equation 130

#### H. Step 8: Construct the observable for the composite system

Now that we have solved the entire system's state vector, we can calculate the measured time-domain NMR signal with the following code below.

```
S=np.matmul(O, sigma)[0][0].real
```

Fig. 9. Code to calculate the measured time-domain NMR signal

Within this code,  $O$  is a row matrix and stores the observable for the composite system. To calculate the matrix, first convert the matrix representations of the observables for the molecules into their row forms as explained in section K.

For our specific example, the observable for  $A = NH_3$  is represented as  $\gamma_{15} N I_{1z} + \gamma_{1H} (I_{2z} + I_{3z} + I_{4z} + I_{5z})$ , where as the observable for  $AB = NH_4^+$  is represented as  $\gamma_{15} N I_{1z} + \gamma_{1H} (I_{2z} + I_{3z} + I_{4z})$ . Once again,  $\gamma$  represents the gyromagnetic ratio as defined before. Specifically  $\gamma_{15} N = -27.126 \times 10^6 T^{-1} s^{-1}$ , while  $\gamma_{1H} = 267.522 \times 10^6 T^{-1} s^{-1}$  [5]. Next the  $O$  matrix is calculated in code by concatenating the two row matrices as shown below.

#### I. Step 9: Simulation of the spectra

Now the following is the code to simulate the time-domain NMR signal.

```
Uevol = expm(M*dt)
for n in range(N_steps):
    S[n]=np.matmul(O, sigma)[0][0].real # calculate the measured signal
    sigma = np.matmul(Uevol, sigma) # Evolve the system for dt
```

Fig. 10. Code to simulates the time-domain NMR)

This is done by measuring and storing the signal at each point within the array denoted  $S$ , where  $N\_steps$  represents the total number of steps for entire the simulation. Finally, the NMR spectral is simulated by taking a Fourier Transform of the time-domain data that was stored before in the matrix  $S$  as shown below.

```
ZF = 32768 # Define the zero filling factor
xf = np.arange(-Bandwidth/2, Bandwidth/2, Bandwidth/ZF) # Calculate the frequency axis

# Implement the zero filling of the FID data
S_ZF = np.zeros(ZF)
S_ZF[:N_steps] = S

# Implement the Fourier transformation
F[n] = np.real(fft(S_ZF)) # Perform FFT
F[n] = scipy.fft.fftshift(S[n]) #Apply frequency shift
```

Fig. 11. Code that simulates the NMR spectral by taking a Fourier transform.

Lastly, the results of the following computations are graphed and shown below.

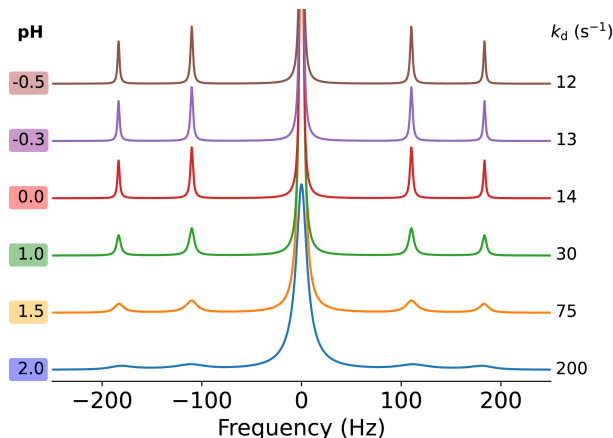


Fig. 12. NMR Spectra

## VI. DISCUSSION AND CONCLUSIONS

In summary, the goal of this paper was to demonstrate the essential tools of linear algebra for simulation of NMR specifically we use applications of bra-ket notation, Kronecker product, and operators as well as superoperators in Hilbert and Liouville space. We apply this principles for the simulation of the association and dissociation of the ammonium compound  $NH_4^+$ . Our approach involved the development of matrix representations for the Hamiltonian, relaxation, and chemical exchange super-operators within the subspace the Liouville space. This advanced mathematical modeling allowed for a more precise and comprehensive simulation of the NMR spectra in low magnetic fields ranging.

Our original exploration started with our broad original question of how to apply various matrix techniques to physical chemistry, specifically with regards to simulating NMR. This started with us familiarizing ourselves with linear algebra notation that was used within field. Although most of the linear algebra concepts discussed within the paper were concepts we already knew from class or were natural extension from material from class, we still need to parse in this information in an unfamiliar notation. However, after familiarizing ourselves with the notation we made a lot interesting discovers and connections with regards content of the paper and the material discussed in class.

Specifically we discovered many interesting manipulations of the existing matrix concepts we already knew. For example



the bra-ket notation introduced within this project was an interesting step from how we have traditionally represent row and column vectors. Furthermore we extend our knowledge of spaces and subspaces when using operators and applying them in context to quantum mechanical systems. Specifically, we thought the concept of a superoperator was really interesting, and a natural extension to the work we did with operators in class. Also we discovered many of the practical applications for many of the existing material we had learned in class. For example it was nice seeing the application of topics such as computing the kernel (which the paper called the null space), matrix exponentials, and the practical application and changing of various bases.

As for our results, the physical results were more or less expected. Despite some difficulties in the formatting of the various matrices and then our results, we produced results that were in line with our paper's conclusions and results.

Moreover, the application of linear algebra tools in this context exemplifies the intersection of mathematics and physical chemistry, showcasing how theoretical mathematical concepts can be effectively applied to solve practical problems in chemical analysis. This interdisciplinary approach is not only beneficial for advancing our theoretical understanding but also has practical implications in improving the techniques and methodologies used in NMR spectroscopy.

In summary, our study not only sheds light on the complex interactions within chemically exchanging systems as observed through NMR spectroscopy but also highlights the immense potential of linear algebra as a powerful tool in scientific research. As for possible future work to be done, we focused mainly on the low-field methods, so future work could be done into looking into the high field as well the Signal amplification by reversible exchange (SABRE) numerical methods and linear algebra techniques. Furthermore, future work could be done on more complex chemical system, using these linear algebra techniques to simulate other particles. Overall, exploration of the applications of matrix methodology to chemical exchange of nuclear magnetic resonance (NMR) was challenging but insightful and fruitful experience for all of us.

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## Appendix A: Code

```
[18]: import numpy as np
import scipy
from math import sqrt
from scipy.linalg import expm
from scipy.fft import fft
import matplotlib.pyplot as plt
```

```
[19]: def Angular_Momentum_Operators(N):
    """
    Angular_Momentum_Operator produce the 4-D matrices containing all the
    ↪ individual spin angular momentum operators.

    :param N: "N" is the number of spin-1/2s of the molecule

    """

    #Generate a empty 4-D matrix with the dimension (N,3,2^N,2^N)
    I = np.empty((N, 3, 2 ** N, 2 ** N), dtype=np.complex128)

    #single spin-1/2 angular momentum operators
    s_x = np.array([[0, 1 / 2],
                    [1 / 2, 0]])

    s_y = np.array([[0, -1j / 2],
                    [1j / 2, 0]])

    s_z = np.array([[1 / 2, 0],
                    [0, -1 / 2]])

    I_1 = np.array([[1, 0],
                    [0, 1]])

    for i in range(N):
        Ix_current = 1
        Iy_current = 1
        Iz_current = 1
        for j in range(N):
            if j == i:
                Ix_current = np.kron(Ix_current, s_x)
                Iy_current = np.kron(Iy_current, s_y)
                Iz_current = np.kron(Iz_current, s_z)
            else:
                Ix_current = np.kron(Ix_current, I_1)
                Iy_current = np.kron(Iy_current, I_1)
                Iz_current = np.kron(Iz_current, I_1)
```

```

        I[i][0] = Ix_current
        I[i][1] = Iy_current
        I[i][2] = Iz_current
    return I

```

```

[20]: #chemical kinetic constant
K_A = 6*1e-10; # NH3 + H+ <--> NH4+

#pH
pH=np.array([-0.5, -0.3, 0.0, 1, 1.5, 2.0])

#Dissociation rates
kd=np.array([12, 13, 14, 30, 75, 200])

#W=[NH4+]/[NH3]
W=10**(-pH)/K_A;

```

```

[46]: # gyromagnetic ratios in unit of Hz/Tesla
gamma_15N = -4.316
gamma_1H = 42.577

#scalar J-couplings in unit of Hz
J_HH = -16.9; #H-H
J_NH = -73.4; #N-H

#specify the Hilbert space of ammonia: NHHH
N_NH3 = 4

#generate the angular momentum operators of ammonia
S_NH3 = Angular_Momentum_Operators(N_NH3)

#generate the Hamiltonian of ammonia
J0_NH3 = np.array([[0,J_NH,J_NH,J_NH],
                   [0, 0,J_HH,J_HH],
                   [0, 0, 0,J_HH],
                   [0, 0, 0, 0]])

H_NH3 = 2*np.pi*np.einsum('ij,iamk,jakn->mn',J0_NH3,S_NH3,S_NH3)

#generate the Hamiltonian superoperator of ammonia
Id_NH3 = np.eye(2**N_NH3)
HS_NH3 = np.kron(H_NH3,Id_NH3)-np.kron(Id_NH3,H_NH3.transpose())

#generate the relaxation superoperator of ammonia
T1_NH3=np.array([5,1,1,1]) #in unit of second

```

```

R_NH3 = np.einsum('i,iamn,iaqp->mpnq',1/T1_NH3,S_NH3,S_NH3) .
↳reshape(4**N_NH3,4**N_NH3)-3/4*np.eye(4**N_NH3)*np.sum(1/T1_NH3)

#Construct the Liouvillian for ammonia
L_NH3 = -1j*HS_NH3+R_NH3

#specify the Hilbert space of ammonium: NHHHH+
N_NH4 = 5

#generate the angular momentum operators of ammonium
S_NH4 = Angular_Momentum_Operators(N_NH4)

#generate the Hamiltonian of ammonium
JO_NH4 = np.array([[0,J_NH,J_NH,J_NH,J_NH],
                   [0, 0,J_HH,J_HH,J_HH],
                   [0, 0, 0,J_HH,J_HH],
                   [0, 0, 0, 0,J_HH],
                   [0, 0, 0, 0, 0]])
H_NH4 = 2*np.pi*np.einsum('ij,iamk,jakn->mn',JO_NH4,S_NH4,S_NH4)

#generate the Hamiltonian superoperator of ammonium
Id_NH4 = np.eye(2**N_NH4)
HS_NH4 = np.kron(H_NH4,Id_NH4)-np.kron(Id_NH4,H_NH4.transpose())

#generate the relaxation superoperator of ammonium
T1_NH4=np.array([5,1,1,1,1]) #in unit of second
R_NH4 = np.einsum('i,iamn,iaqp->mpnq',1/T1_NH4,S_NH4,S_NH4) .
↳reshape(4**N_NH4,4**N_NH4)-3/4*np.eye(4**N_NH4)*np.sum(1/T1_NH4)

#construct the Liouvillian for ammonium
L_NH4 = -1j*HS_NH4+R_NH4

#Generate the identity matrices for molecule fragments X,Y,Z for all cases:
I2,I4,I8,I16 = np.eye(2),np.eye(4),np.eye(8),np.eye(16)

# Generate the partial Trace Superoperator
Tr1 = np.einsum("ij,yk,lm,yn->iljkmn",I16,I2,I16,I2).reshape(16**2,32**2)
Tr2 = np.einsum('ij,yk,lm,np,yq,rs->ilnrjkmpqs',I8,I2,I2,I8,I2,I2) .
↳reshape(16**2,32**2)
Tr3 = np.einsum('ij,yk,lm,np,yq,rs->ilnrjkmpqs',I4,I2,I4,I4,I2,I4) .
↳reshape(16**2,32**2)
Tr4 = np.einsum('ij,yk,lm,np,yq,rs->ilnrjkmpqs',I2,I2,I8,I2,I2,I8) .
↳reshape(16**2,32**2)
Tr = 1/4*(Tr1+Tr2+Tr3+Tr4)

```

```

# Generate the Kronecker Product Superoperator
rho = I2/2
Kron1 = np.einsum("ij,ky,lm,np,qY,rs,yY->iklnqrjumps",I2,I2,I8,I2,I2,I8,rho) .
    ↳reshape(32**2,16**2)
Kron2 = np.einsum("ij,ky,lm,np,qY,rs,yY->iklnqrjumps",I4,I2,I4,I4,I2,I4,rho) .
    ↳reshape(32**2,16**2)
Kron3 = np.einsum("ij,ky,lm,np,qY,rs,yY->iklnqrjumps",I8,I2,I2,I8,I2,I2,rho) .
    ↳reshape(32**2,16**2)
Kron4 = np.einsum("ij,ky,lm,nY,yY->iklnjnm",I16,I2,I16,I2,rho) .
    ↳reshape(32**2,16**2)
Kron = 1/4*(Kron1+Kron2+Kron3+Kron4)

# Generate the initial density operators for both molecules
rho_NH3 = gamma_15N*S_NH3[0][2]+gamma_1H*(S_NH3[1][2]+S_NH3[2][2]+S_NH3[3][2])
rho_NH4 = ␣
    ↳gamma_15N*S_NH4[0][2]+gamma_1H*(S_NH4[1][2]+S_NH4[2][2]+S_NH4[3][2]+S_NH4[4][2])

# Generate the observables for both molecules
O_NH3 = gamma_15N*S_NH3[0][2]+gamma_1H*(S_NH3[1][2]+S_NH3[2][2]+S_NH3[3][2])
O_NH4 = ␣
    ↳gamma_15N*S_NH4[0][2]+gamma_1H*(S_NH4[1][2]+S_NH4[2][2]+S_NH4[3][2]+S_NH4[4][2])

# Convert the observables into the row forms ( $\langle O^\dagger \rangle$ )
O_NH3 = O_NH3.flatten('F')
O_NH4 = O_NH4.flatten('F')

#Generate the row of the obserbale for the entire system by connecting the␣
    ↳observable for each molecule
O = np.block([O_NH3, O_NH4])

```

```

[6]: Bandwidth = 600 # Define the bndwidth in unit of Hz
N_steps = 4096 # Define the number of steps for the simulation
dt = 1/Bandwidth # Define the time step for tthe simulation (in unit of second)
S = np.empty(N_steps) # Apply for memory for storing the Frquency domain data
ZF = 32768 # Define the zero-filling factor

xf = np.arange(-Bandwidth/2,Bandwidth/2,Bandwidth/ZF) # Calculate the frequency␣
    ↳axis
F = np.empty((6,ZF)) # Apply for memory for storing the Spectra

for n in range(6):

```

```

# Generate the coefficient matrix for the composite system,
→  $\tilde{k}_a = k_d W$ 
M=np.block([[L_NH3-kd[n]*W[n]*np.eye(4**N_NH3), kd[n]*Tr],[kd[n]*W[n]*Kron,
→ L_NH4-kd[n]*np.eye(4**N_NH4)]])

#Generate the time evolution operator for the composite system
U_evol = expm(M*dt)

# Generate the initial concentration-normalized density operators for both
→ molecules, assume  $[NH_4^+]=1$  and  $[NH_3]=1/W$  for simplicity
sigma_NH3 = 1/W[n]*rho_NH3
sigma_NH4 = rho_NH4

# Convert the density matrices into density columns for both molecules
sigma_NH3 = sigma_NH3.flatten().reshape((-1, 1))
sigma_NH4 = sigma_NH4.flatten().reshape((-1, 1))

# Generate the initial state vector for the entire system by connecting the
→ density column for each molecule
sigma_0 = np.block([[sigma_NH3],[sigma_NH4]])

#Calculate the time domain NMR data
sigma = sigma_0
for n1 in range(N_steps):
    S[n1]=np.matmul(0,sigma)[0][0].real
    sigma = np.matmul(U_evol,sigma)

# Implement the zero-filling to time domain data
S_ZF = np.zeros(ZF)
S_ZF[:N_steps] = S

# Implement the Fourier transformation
F[n] = np.real(fft(S_ZF))
F[n] = scipy.fft.fftshift(F[n]) #Apply frequency shift

```

```

[57]: bbox_color = ['blue','orange','green','red','purple','brown']
fig, ax = plt.subplots()

for n in range(6):
    ax.plot(xf,F[5-n]+n*2e5+1e4) #F[5-n]+n*2e5+1e5
    ax.text(255, n*2e5+2.5e4, f'{kd[5-n]}',fontsize=12) #n*2e5+2.5e4
    ax.text(-290, n*2e5+2.5e4, f'{pH[5-n]:4.1f}',fontsize=12,
→ bbox=dict(facecolor=bbox_color[n], edgecolor='None', alpha=0.4,
→ boxstyle='round, pad=0.2')) #n*2e4+2.5e4

ax.set_xlim(-250, 250)

```

```

ax.set_ylim(0,1.3*1e6) #1.3*1e6
ax.set_xlabel('Frequency (Hz)',fontsize=16)

ax.spines['top'].set_visible(False)
ax.spines['right'].set_visible(False)
ax.spines['left'].set_visible(False)

ax.get_yaxis().set_ticks([])

ax.text(250, 1.2*1e6, r'$k_{\rm d}$ (s$^{-1}$)',fontsize=12) # 1.2*1e6
ax.text(-285, 1.2*1e6, 'pH',fontsize=12, weight='bold') # 1.2*1e6

ax.tick_params(axis='both', which='major', labelsize=16)

plt.show()
fig.savefig('NH4_ZF.pdf', bbox_inches='tight')

```

