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ARTICLE

Revisiting Applications of Mathematics in Chemistry: Linear Algebra

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A B S T R A C T

Linear algebra is the study of vectors in vector spaces, and linear transformation in that vector spaces. In this paper, we review and extend how some phenomena, system, and even information in chemistry can be described and/or modelled as vectors or matrices, thus allowing the use of linear algebra methods in the description of the system. In particular, we show how first order chemical kinetic mechanism, multiple linear regression, quantum states, and chemical graph theory can all described using matrices.

Keywords: Linear Algebra, Matrices, Vectors, Eigenvalues, Differential Equation.

A B S T R A K

Aljabar linier merupakan bidang ilmu yang mengkaji vektor di dalam ruang vektor, dan transformasi linier dalam ruang vektor tersebut. Dalam naskah ini kami meninjau ulang, dan menambahkan bagaimana beberapa fenomena, sistem, maupun informasi dapat dinyatakan sebagai vektor atau matriks, sehingga dapat digunakan metode aljabar linier untuk mendeskripsikan sistem tersebut. Kami menunjukkan bahwa mekanisme kinetika kimia orde 1, regresi multilinier, representasi keadaan kuantum, dan aplikasi teori graf dalam kimia dapat direpresentasikan sebagai matriks.

Kata Kunci: Aljabar Linear, Matriks, Vektor, Swanilai, Persamaan Diferensial.

INTRODUCTION

In modern mathematics, subjects of study are usually categorized into what the object that was studied, and what methods was used in that study. With object of study include harmonic functions, topological spaces, algebraic structure, and vector spaces. The study of vector spaces and linear transformations in said space is called linear algebra. Formally, vector space V over a scalar field F is a set with 2 binary operations $(+,\times)$ that fulfill these following axioms

1. $(V, +)$ is an abelian group
2. $(\forall a, b \, \epsilon \, F)(\forall v \, \epsilon \, V) \, (a(bv) = (ab)v)$
3. $(\exists \, 1 \, \epsilon)(\forall v) \, (1v = v)$
4. $(\forall a, b \, \epsilon \, F)(\forall v \, \epsilon \, V) \left((a + b)v = av + bv\right)$
5. $(\forall a \, \epsilon \, F)(\forall u, v \, \epsilon \, V)(a(u + v) = au + av)$

Elements of V will then called vectors and elements of F will then called scalars.

Within this vector spaces we can also defined transformation from a certain vector to another vector. And if a certain transformation T fulfill these properties [1-2]

$$T(au + bv) = T(au) + T(bv) = aT(u) + bT(v)$$

Despite being very general and abstract in its definitions, in most cases, vectors, scalars, and even transformation in a given vector space is represented as matrices with scalar is represented as 1×1 matrix, vector as column matrix, and linear transformation in a given space as square matrix, and linear transformation between spaces is given by rectangular matrix with appropriate dimension. Due to this, linear algebra is widely use in formal science for representation of state, and physical science to model the properties and behavior of linear system.

In this paper, we will revisit some of the simplest applications of linear algebra which include First-Order Chemical Kinetic Mechanism [3], Multiple Linear Regression [4-7], Representation of Quantum States [8-11], and Graph Theory

FIRST-ORDER CHEMICAL KINETICS MECHANISM

Chemical kinetics is the study of reaction mechanism, reaction rates, and rate laws. For a simple elementary reaction

$$aA + bB + \cdots \rightarrow Products$$
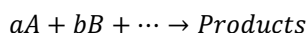
The rate law is given by

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]^a[B]^b \ldots = \prod_n [R]_n{}^{r_n}$$

From the given equation, it is easy to conclude the general rate law is by no mean linear. However, for some special cases, there are system of complex reactions for which every term in it is linear. Examples of these reactions include consecutive reaction and opposing reaction.

Consecutive Reaction

Simple generic consecutive reaction will be given by

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
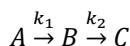
The rate laws for each species if given by

$$\frac{d}{dt}[A] = -k_1[A]$$

$$\frac{d}{dt}[B] = k_1[A] - k_2[B]$$

$$\frac{d}{dt}[C] = k_2[B]$$

It can be seen that all equations are actually linear, and should be solvable using linear algebra. Those equations can be combined into a single equation

$$\frac{d}{dt}\begin{pmatrix} [A] \\ [B] \\ [C] \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix}\begin{pmatrix} [A] \\ [B] \\ [C] \end{pmatrix}$$

$$\frac{d}{dt}\vec{R} = K\vec{R}$$

Where, $\vec{R}$ is the concentration vectors, and K is the constants matrix. Through abuse of notations, we can write the solution for this equation is given by

$$\vec{R} = e^{Kt}\vec{R}(0)$$

Where, e^K is exponential of a matrix which is given by

$$\exp\left(\begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix}t\right) = P\begin{pmatrix} e^{\lambda_1 t} & 0 & 0 \\ 0 & e^{\lambda_2 t} & 0 \\ 0 & 0 & e^{\lambda_3 t} \end{pmatrix}P^{-1}$$

Where, the columns of P are the eigenvectors of matrix K with λ_n is the corresponding eigenvalues of the eigenvectors.

This exponential function can also be replaced by any function that can be represented by power series.

$$f\begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} = P\begin{pmatrix} f(\lambda_1) & 0 & 0 \\ 0 & f(\lambda_2) & 0 \\ 0 & 0 & f(\lambda_3) \end{pmatrix}P^{-1}$$

The matrix exponential for consecutive reaction is given by

$$e^K = P\begin{pmatrix} e^0 & 0 & 0 \\ 0 & e^{-k_1} & 0 \\ 0 & 0 & e^{-k_2} \end{pmatrix}P^{-1}$$

$$P = \begin{pmatrix} 0 & \dfrac{k_1 - k_2}{k_2} & 0 \\ 0 & -\dfrac{k_1}{k_2} & -1 \\ 1 & 0 & 1 \end{pmatrix}$$

And assuming that only A has non-zero initial concentration, this following equation

$$\begin{pmatrix} e^{-k_1 t} & 0 & 0 \\ \dfrac{k_1(e^{-k_2 t} - e^{-k_1 t})}{k_1 - k_2} & e^{-k_2 t} & 0 \\ \dfrac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} + 1 & -e^{-k_2 t} + 1 & 1 \end{pmatrix}\begin{pmatrix} [A]_0 \\ 0 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} [A] \\ [B] \\ [C] \end{pmatrix} = \begin{pmatrix} [A]_0 e^{-k_1 t} \\ [A]_0 k_1\left(\dfrac{e^{-k_2 t} - e^{-k_1 t}}{k_1 - k_2}\right) \\ [A]_0\left(\dfrac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} + 1\right) \end{pmatrix}$$
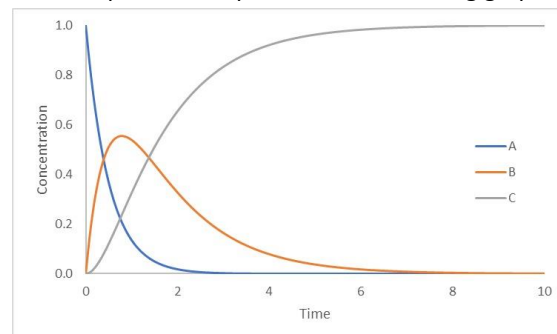
Which if plotted will produce this following graph.

Figure 1. Concentration as function of time in consecutive reaction

Opposing Reaction

Simplest opposing chemical reaction is given by

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

And the rate law will be given by

$$\frac{d}{dt}[A] = -k_1[A] + k_{-1}[B]$$

$$\frac{d}{dt}[B] = k_1[A] - k_{-1}[B]$$

Analogous with the consecutive reaction, these rate laws can be combined into

$$\frac{d}{dt}\begin{pmatrix}[A]\\[B]\end{pmatrix} = \begin{pmatrix}-k_1 & k_{-1}\\ k_1 & -k_{-1}\end{pmatrix}\left(\begin{pmatrix}[A]\\[B]\end{pmatrix}\right)$$

With matrix exponential given by

$$e^{Kt} = \begin{pmatrix}\frac{k_{-1}}{k_1} & -1\\ 1 & 1\end{pmatrix}\begin{pmatrix}e^{0t} & 0\\ 0 & e^{-(k_1+k_{-1})t}\end{pmatrix}\begin{pmatrix}\frac{k_{-1}}{k_1} & -1\\ 1 & 1\end{pmatrix}^{-1}$$

Therefore, the solutions for the rate law, assuming only A has non-zero initial concentration, the equation can be written as

$$\begin{pmatrix}[A]\\[B]\end{pmatrix} = \left(\frac{[A]_0}{k_1 + k_{-1}}\right)\begin{pmatrix}k_1 e^{-(k_1+k_{-1})t} + k_{-1}\\ k_1 - k_{-1}e^{-(k_1+k_{-1})t}\end{pmatrix}$$
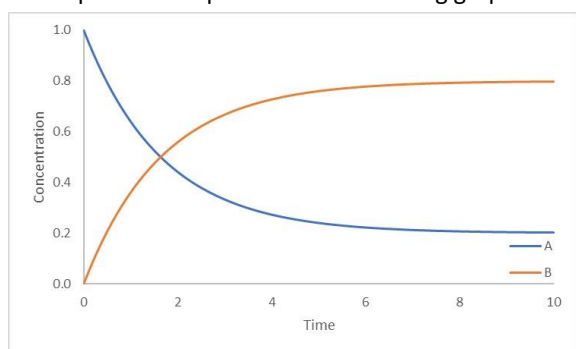
And if plotted will produce this following graph

Figure 2. Concentration as function of time in opposing reaction

MULTIPLE LINEAR REGRESSION

Regression analysis is a very important method of data analysis in chemistry, because a lot of data can be simplified into a simple linear regression model. However, there are data that simply cannot be fitted into simple linear regression model and have to be reduced into multiple linear regression model instead. Generalization from simple linear regression into multiple linear regression while cannot be considered to be complicated, it is by no mean can be considered to be trivial. Consider this following data from screened Coulombic (-Yukawa) potential (V_Y) as function of distance (r)

Table 1. Potential as function of distance in certain system

r	V_Y (×10⁻⁶)
2.0	-20.1
4.0	-7.56
6.0	-3.80
8.0	-2.14
10	-1.29
12	-0.811

The equation for this potential is given by

$$V_Y = -g^2 \frac{e^{-\alpha m r}}{r}$$

Where, g is the coupling constant, α is the mass scaling constant, and m is the mass of the gauge boson – which is zero for photon, and non-zero for weak interaction.

Linearization of that equation using logarithm will produce

$$\ln(-V_Y) = \ln\left(g^2 \frac{e^{-\alpha m r}}{r}\right)$$

$$\ln(-V_Y) = \ln(g^2) + \ln\left(\frac{1}{r}\right) + \ln(e^{-\alpha m r})$$

$$\ln(-V_Y) = \ln(g^2) - \ln(r) - \alpha m r$$

It can be seen that the equation while depend only to distance, there are 2 functions for distance which are linear and logarithmic, therefore simple linear regression will not be able to compute the parameters. By rewriting the data in Table 1 will produce

Table 2. Linearized data for regression

$\ln(-V_Y)$	$\ln(r)$	r
-10.815	0.693	2.0
-11.793	1.386	4.0
-12.481	1.792	6.0
-13.055	2.079	8.0
-13.561	2.303	10
-14.025	2.485	12

This data table can split into 2 matrices, which are the Y matrix and X matrix

$$Y = \begin{pmatrix}-10.815\\ -11.793\\ -12.481\\ -13.055\\ -13.561\\ -14.025\end{pmatrix}$$

$$X = \begin{pmatrix}1 & 0.693 & 2.0\\ 1 & 1.386 & 4.0\\ 1 & 1.792 & 6.0\\ 1 & 2.079 & 8.0\\ 1 & 2.303 & 10\\ 1 & 2.485 & 12\end{pmatrix}$$

Due to the linearized equation of the Yukawa potential, the relation between these matrices can be written as

$$\begin{pmatrix}-10.815\\ -11.793\\ -12.481\\ -13.055\\ -13.561\\ -14.025\end{pmatrix} = \begin{pmatrix}1 & 0.693 & 2.0\\ 1 & 1.386 & 4.0\\ 1 & 1.792 & 6.0\\ 1 & 2.079 & 8.0\\ 1 & 2.303 & 10\\ 1 & 2.485 & 12\end{pmatrix}\begin{pmatrix}\beta_0\\ \beta_1\\ \beta_2\end{pmatrix} + \begin{pmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{pmatrix}$$

$$Y = X\beta + \varepsilon$$

Where, ε is the error vector, β is the coefficient vector, and X is the independent variable matrix. The addition of ones column into the matrix to account for the constant term in the equation. If for some reason the constant term does not exist, then the constant term can be removed from the matrix. However, in this example, there is a constant

term of $\ln(g^2)$. By trying to minimize the value of $\varepsilon^T \varepsilon$, the β vector is given by

$$\beta = (X^T X)^{-1} X^T Y$$

$$\beta = \begin{pmatrix} -9.8437 \\ -1.003 \\ -0.141 \end{pmatrix} = \begin{pmatrix} \ln(g^2) \\ -1 \\ -\alpha m \end{pmatrix}$$

Substituting these parameters back into the equation for Yukawa potential and calculating the interaction using it will produce

Table 3. Comparison between regression results with data

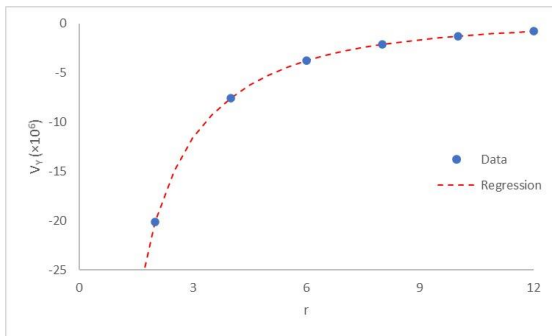| r	V_Y ($\times 10^{-6}$)	
	Data	Regression
2.0	-20.1	-20.1
4.0	-7.56	-7.56
6.0	-3.80	-3.79
8.0	-2.14	-2.14
10	-1.29	-1.29
12	-0.811	-0.810

Figure 3 Comparison between data and regression results

REPRESENTATION OF QUANTUM STATE

Wavefunction and Operator

Quantum mechanics is the model that is used for quantum system. The most widely used formulation of this Schrodinger wave mechanics, in which the state of the system is described as wavefunctions and the observable of the system is described as linear operator, and this description is summarized in linear second order homogenous partial differential equation, which is also an eigenvalue equation.

$$\hat{H}|\psi\rangle = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(x) \right] |\psi\rangle = i\hbar \frac{\partial}{\partial t} |\psi\rangle = E|\psi\rangle$$

Solutions to this equation is fully defined by the Hamiltonian of the system. If the wavefunction is already normalized, then

$$\langle \psi_m | \psi_n \rangle = \int_{all\ space} \psi_m^* \psi_n \, d\tau = \delta_{mn}$$

And the expected value of observable with operator $\hat{\Omega}$ will be given by

$$\langle \psi | \hat{\Omega} | \psi \rangle = \int_{all\ space} \psi_m^* \hat{\Omega} \psi_n \, d\tau$$

Despite the simplicity and the fact that this formulation is visualizable, it is easier to understand the operator form of this equation as well as its properties is we actually understand it as matrices and vectors.

For example, consider particle in 1-D box system. The potential of the system is given by

$$V(x) = \begin{cases} 0, inside\ the\ box \\ \infty, outside\ the\ box \end{cases}$$

And the energy and wavefunction of the system is given by

$$E_n = n^2 \frac{\pi^2 \hbar^2}{2mL^2} = n^2 E_1$$

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$$

We can choose to describe this system with these following infinite matrices

$$\hat{H} = \begin{pmatrix} E_1 & 0 & 0 & \cdots \\ 0 & E_2 & 0 & \cdots \\ 0 & 0 & E_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$$|\psi_n\rangle = \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$$

$$\langle \psi | = (|\psi_n\rangle^*)^T$$

Where nth component of $|\psi_n\rangle$ is 1 and zero everywhere else. It is then trivial to show that

$$\langle \psi_n | \psi_n \rangle = \begin{pmatrix} \cdots & 0 & 1 & 0 & \cdots \end{pmatrix} \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} = 1$$

And

$$\langle \psi_n | \hat{H} | \psi_n \rangle$$

$$= \begin{pmatrix} \cdots & 0 & 1 & 0 & \cdots \end{pmatrix} \begin{pmatrix} E_1 & 0 & 0 & \cdots \\ 0 & 4E_1 & 0 & \cdots \\ 0 & 0 & 9E_1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} = E_n$$

It is also trivial to show that for quantum harmonic oscillator the Hamiltonian is given by

$$\hat{H} = \begin{pmatrix} E_1 & 0 & 0 & \cdots \\ 0 & E_2 & 0 & \cdots \\ 0 & 0 & E_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} = \begin{pmatrix} \frac{1}{2}\hbar\omega & 0 & 0 & \cdots \\ 0 & \frac{3}{2}\hbar\omega & 0 & \cdots \\ 0 & 0 & \frac{5}{2}\hbar\omega & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

This formulation of quantum states as vectors in infinite dimensional space also explain the need for Hilbert space as the space of quantum states, and how operators are

basically just linear transformation in infinite dimensional complex space.

Density Matrix

Density matrix is an alternative – and arguably – better way of representing the state of a quantum system. Unlike wavefunctions or state vectors, density matrix is more general because its can be used to represent not only superposition of pure states, but combinations of mixed quantum states. Consider a general pure state $|\psi\rangle$, the density matrix of that state is given by

$$\rho = |\psi\rangle\langle\psi|$$

And if the system is defined by multiple states and we do not have the information for the exact states of the system, the density matrix of that system can be written as

$$\rho = \sum_n |\psi_n\rangle\langle\psi_n|$$

With the hidden information that we lack is measured as von Neumann entropy is defined as

$$H = tr(\rho \ln \rho)$$

GRAPH THEORY

Graph theory is the study of graphs, which are nodes (vertices) connected by edges. Formally, graph $G(V, E)$ is defined as collection of vertices V and collection of edges E.

Graph theory is quite useful in chemistry due to its invariance under permutation (re-labelling) and how a graph is fully defined by connections between just like most chemical compounds are fully defined by bonds between the atoms. Consider molecule of isobutane
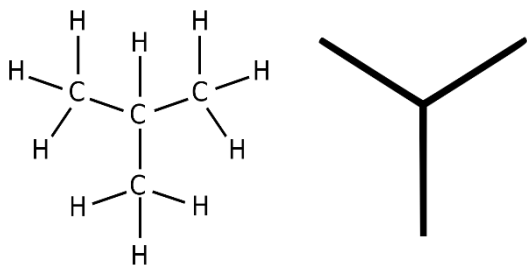

Figure 4 Structure of isobutane

This molecular structure can be described as a graph with vertices representing the atoms and edges representing bond.
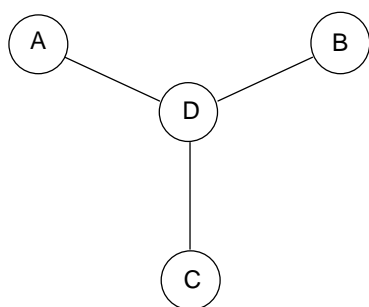

Figure 5 Graph representation of isobutane

This graph can then be represented as square matrix called adjacency matrix. Within this matrix, each row and column correspond to a specific vertex, and the matrix elements is 1 if there is an edge between the vertices, and 0 everywhere else. The graph is Figure 5 can then be represented as this following matrix

$$A = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \\ 1 & 1 & 1 & 0 \end{pmatrix}$$

It is important to note that this adjacency matrix or any matrix produced from a graph is not – in general – invariant to re-labelling. However, due to permutation invariance, graph spectra (set of its eigenvalues) are invariant under re-labelling. This is why most application of graph theory usually used eigenvalue of the graph or any other invariant of a graph. An example of this energy of the graph which defined as sum of absolute value of

$$\mathcal{E} = \sum_{v \in V} |\lambda_v|$$

Which for graph of isobutane is $2\sqrt{3}$.

CONCLUSIONS.

We show how linear algebra as a branch of mathematics can be used in chemistry as it can be used to solve system of linear differential equation, calculating the coefficients of variables in multiple linear regression, as well as representation of chemical system, especially through state vectors, density matrices, and adjacency graphs.

We also show how some properties of matrices such as its eigenvalues, eigenvectors, and its trace can used in to calculate properties of chemical system. Eigenvalues and eigenvectors in particular can be used in matrix diagonalization that was used in calculating matrix function.

AUTHORS CONTRIBUTION

HAA, HH, and FK all involved in the writing of the paper. HAA visualized most of the figures presented in the paper.

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