CHEM1030 - Week 25 Lecture - eigensystems
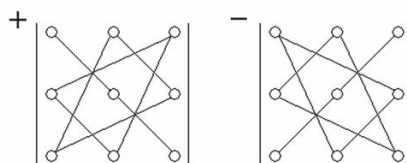
Chapters 17 and 19 of Steiner, "The Chemistry Maths Book", 2nd edition.

Determinants

Matrix determinant is an auxiliary function that often occurs in matrix algebra. It is defined in terms of products of matrix elements. For 2x2 and 3x3 matrices the expressions are:

$$\det\begin{pmatrix} a & b \\ c & d \end{pmatrix} = ad - bc, \qquad \det\begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix} = aei + bfg + cdh - ceg - bdi - afh \qquad (1)$$

The following diagram is useful for memorizing the element multiplication order in the 3x3 case:

Determinants of larger matrices can be expressed *via* the determinants of their submatrices – see Section 17.3 in Steiner. Determinants are useful as indicators of various matrix properties, which in this course will be given without formal proof:

1. The inverse matrix exists only for matrices with a non-zero determinant.

2. The equation $\mathbf{A}\vec{x} = 0$ can only have non-zero solutions if $\det \mathbf{A} = 0$.

3. A real 3x3 matrix with a determinant of +1 is a rotation. If the determinant is −1, it is a rotation preceded or followed by a reflection.

In physics, wavefunctions of fermionic systems are formulated in terms of determinants because the determinant changes sign when any pair of matrix rows or columns is swapped. This property happens to coincide with the particle permutation property imposed on fermions by the Schrödinger equation.

Eigenvalues, eigenvectors and eigenfunctions

It is well known that strings of musical instruments oscillate at specific frequencies, atoms and molecules have specific energy levels, bridges have specific resonances that must be avoided and physical systems in general display reproducible patterns of behaviour and properties that are in some sense intrinsic to those systems. Such properties often correspond to what is called an *eigensystem*.

A non-zero vector $\vec{v}$ is called an eigenvector of a square matrix $\mathbf{A}$ and λ is called the corresponding eigenvalue if $\mathbf{A}\vec{v} = \lambda\vec{v}$. In function spaces, a non-zero function $|f\rangle$ is called an eigenfunction of an operator $\hat{O}$ and λ is called the corresponding eigenvalue if $\hat{O}|f\rangle = \lambda|f\rangle$. The set of all eigenvalues and eigenfunctions / eigenvectors is called the eigensystem of the operator or matrix. Examples:

1. Plane wave functions are eigenfunctions of the coordinate derivative operator:

$$\frac{\partial}{\partial x}\left(\frac{e^{ikx}}{\sqrt{\pi}} \right) = ik\left(\frac{e^{ikx}}{\sqrt{\pi}} \right)$$

2. Sinusoidal oscillations are eigenfunctions of the acceleration operator:

$$\frac{\partial^2}{\partial t^2}\left[\sin(\omega t) \right] = -\omega^2 \left[\sin(\omega t) \right]$$

3. Z axis direction is an eigenvector of the matrix that performs rotations around Z:

$$\begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

4. Atomic orbitals (*s*, *p*, *d*, *f*, …) are eigenfunctions of the energy operator for the hydrogen atom. Time does not permit us to consider them here – look up spherical harmonics and the Laplace operator.

Eigenvectors and eigenfunctions play a fundamental role – solutions to most problems in mathematical physics are formulated in terms of the eigensystems of the corresponding operators.

Eigensystems of matrices

Given a matrix $\mathbf{A}$, we can write the following equation for its eigenvalues and eigenvectors:

$$\mathbf{A}\vec{x} = \lambda\vec{x} \quad \Rightarrow \quad \mathbf{A}\vec{x} = \lambda\mathbf{1}\vec{x} \quad \Rightarrow \quad (\mathbf{A} - \lambda\mathbf{1})\vec{x} = 0 \tag{2}$$

As noted above, this matrix equation only has non-zero solutions if

$$\det(\mathbf{A} - \lambda\mathbf{1}) = 0 \tag{3}$$

which is simply a polynomial equation for λ with the number of solutions that is equal to the dimension of the matrix (we shall skip the proof of this statement here). Solving Equation (3) gives all the eigenvalues that we will enumerate with an index k and call $\{\lambda_k\}$. For each eigenvalue λ_k we can now solve Equation (2) and obtain the corresponding eigenvectors. By convention, they are normalized. Example:

$$\begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \lambda\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \quad \Rightarrow \quad \det\left[\begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} - \lambda\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] = 0$$

Opening up the determinant yields a quadratic equation:

$$\det\left[\begin{pmatrix} -\lambda & 1/2 \\ 1/2 & -\lambda \end{pmatrix}\right] = 0 \quad \Rightarrow \quad \lambda^2 - \frac{1}{4} = 0 \quad \Rightarrow \quad \begin{cases} \lambda_1 = +1/2 \\ \lambda_2 = -1/2 \end{cases}$$

Solving Equation (2) (including the normalization condition) for the first eigenvalue:

$$\begin{cases} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \\ x_1^2 + x_2^2 = 1 \end{cases} \Rightarrow \begin{cases} 1/2\,x_2 = 1/2\,x_1 \\ 1/2\,x_1 = 1/2\,x_2 \\ x_1^2 + x_2^2 = 1 \end{cases} \Rightarrow \begin{cases} x_1 = x_2 \\ x_1^2 + x_2^2 = 1 \end{cases} \Rightarrow \begin{cases} x_1 = \dfrac{1}{\sqrt{2}} \\ x_2 = \dfrac{1}{\sqrt{2}} \end{cases}$$

Note that the system will always contain one redundant equation – this is a subtle consequence of forcing the determinant to be zero in Equation (3). Doing the same for the second eigenvalue yields:

$$\begin{cases} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = -\frac{1}{2}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \\ x_1^2 + x_2^2 = 1 \end{cases} \Rightarrow \begin{cases} 1/2\,x_2 = -1/2\,x_1 \\ 1/2\,x_1 = -1/2\,x_2 \\ x_1^2 + x_2^2 = 1 \end{cases} \Rightarrow \begin{cases} x_1 = -x_2 \\ x_1^2 + x_2^2 = 1 \end{cases} \Rightarrow \begin{cases} x_1 = +\dfrac{1}{\sqrt{2}} \\ x_2 = -\dfrac{1}{\sqrt{2}} \end{cases}$$

The final answer is:

$$\left\{\lambda_1 = \frac{1}{2},\ \vec{x}_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}\right\}, \quad \left\{\lambda_2 = -\frac{1}{2},\ \vec{x}_1 = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}\right\}$$

Note that eigenvectors are defined up to a constant multiplier – if $\vec{v}$ is an eigenvector, then for an arbitrary non-zero complex number α, the vector $\alpha\vec{v}$ is also an eigenvector with the same eigenvalue.

The flowchart for the eigenvalue and eigenvector determination can be summarized as follows: (a) solve Equation (3) for λ; (b) for each value of λ, solve Equation (2) for $\vec{x}$ with the condition that $\|\vec{x}\| = 1$; (c) test your answer by computing the following matrix products and testing the following equality:

$$\mathbf{A}\begin{pmatrix} | & | & \\ \vec{x}_1 & \vec{x}_2 & \cdots \\ | & | & \end{pmatrix} = \begin{pmatrix} | & | & \\ \vec{x}_1 & \vec{x}_2 & \cdots \\ | & | & \end{pmatrix}\begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \ddots \end{pmatrix} \tag{4}$$

If this equality holds, the eigenvalues and eigenvectors have been computed correctly.

Eigensystems of quantum mechanical operators

Operators in quantum mechanics are often combinations of differentiation and multiplication. They will all be derived in due course – for now we will simply take the expressions out of the QM textbooks. The procedure for finding eigenvalues and eigenfunctions of differential operators

$$\hat{O}|\psi\rangle = \lambda|\psi\rangle \tag{5}$$

simply amounts to solving the corresponding differential equations. Example ("particle in a box"):

$$\hat{H}|\psi(x)\rangle = E|\psi(x)\rangle, \quad \hat{H} = -\frac{1}{2m}\frac{\partial^2}{\partial x^2}, \quad \begin{cases} \psi(0) = 0 \\ \psi(a) = 0 \end{cases}$$

where E is the energy of the particle (quantum mechanical energies are eigenvalues of certain operators called Hamiltonians), $\hat{H}$ is the Hamiltonian operator and a is the size of the box. After writing down the differential equation explicitly, we obtain:

$$-\frac{1}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E\psi(x) \quad \Rightarrow \quad \frac{\partial^2\psi(x)}{\partial x^2} = -2mE\psi(x)$$

It is clear (we shall skip a lot of formal math here) that the solutions are sines and cosines. In general:

$$\psi(x) = \alpha\cos\left(\sqrt{2mE}\,x\right) + \beta\sin\left(\sqrt{2mE}\,x\right)$$

where α and β are arbitrary numbers. The solution must be zero at $x = 0$, meaning that $\alpha = 0$. We are therefore left with:

$$\psi(x) = \beta\sin\left(\sqrt{2mE}\,x\right)$$

which must also be zero at $x = a$, therefore:

$$\beta\sin\left(\sqrt{2mE}\,a\right) = 0 \quad \Rightarrow \quad \sqrt{2mE}\,a = \pi n \quad \Rightarrow \quad E_n = \frac{\pi^2 n^2}{2ma^2}, \quad n = 1,2,3...$$

where the solution with $n = 0$ has been discarded because it corresponds to there being no particle at all. After substituting the energy expression into the eigenfunction, we get:

$$\psi_n(x) = \beta\sin\left(\frac{\pi nx}{a}\right)$$

The coefficient β should be adjusted so that the function has a unit norm:

$$\langle \psi_n | \psi_n \rangle = \int_0^a \beta^2 \sin^2\left(\frac{\pi n x}{a}\right) dx = 1 \quad \Rightarrow \quad \beta = \sqrt{\frac{2}{a}}$$

And so the final answer is:

$$E_n = \frac{\pi^2 n^2}{2ma^2}, \quad \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi n x}{a}\right), \quad n = 1, 2, 3\ldots$$

As expected for a differential operator, the number of eigenfunction-eigenvalue pairs is infinite.

Week 30 workshop exercises

Steiner, 2nd edition: section 17.8, problems 2-4, 6-9 (using Equation 1 or the schematic given above), 25 (compute the determinant first); section 19.7, problems 4-18, 36-38.

Extra difficulty exercises for the brave

Steiner, 2nd edition: section 17.8, problem 18; section 19.7, problems 21-23.