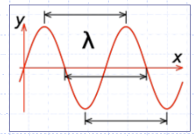
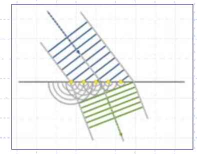
Physical Chemistry

Lecture 11

Waves, Matrices, Operators, and Eigenvalue Equations

Waves



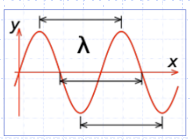


$$\lambda = \frac{\lambda_0}{n(\lambda_0)},$$

λ_0 - wavelength in vacuum

$n(\lambda_0)$ - refractive index of the medium, which varies with wavelength (dispersion)

Wave moving through space



$$y(x,t) = A\cos\big(k(x - vt)\big)$$

Dispersion relation:

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{v}$$

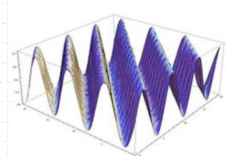
Not simple, because v is a function of ω

Waves in complex notation

Wave equation

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}$$

$$u = Ae^{ikx}e^{-i\omega t}$$



$$k = \frac{2\pi}{\lambda}$$

$$\omega = 2\pi f$$

Matrices

- Matrix: an array of numbers or functions.
- Position in the array is important
  - Labeling of matrix elements requires two indices
- Rank – the number of rows or columns

$$\mathbf{A} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}$$

$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

Special types of matrices

- Square matrix
  - Row rank equal to column rank
- Symmetric matrix **S**
  - Off-diagonal elements across principal diagonal are equal
- Diagonal matrix **D**
  - All off-diagonal elements are zero
- Real matrix **R**
  - All elements are real numbers or real functions
- Complex matrix **C**
  - Some elements are complex numbers or functions
- Transpose of a matrix
  - A matrix formed from another by exchanging elements across the principal diagonal

$$\mathbf{S} = \begin{bmatrix} a_{11} & A & B \\ A & a_{22} & C \\ B & C & a_{33} \end{bmatrix}$$

$$\mathbf{D} = \begin{bmatrix} a_{11} & 0 & 0 \\ 0 & a_{22} & 0 \\ 0 & 0 & a_{33} \end{bmatrix}$$

$$\mathbf{R} = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix}$$

$$\mathbf{C}(x,y) = \begin{bmatrix} 1 & x+iy & 25 \\ x-iy & 3+2i & 44 \\ 6 & 3 & xy \end{bmatrix}$$

Matrix mathematics

- Equality

$$\mathbf{A} = \mathbf{B} \Leftrightarrow a_{ij} = b_{ij}$$

- Additivity and subtraction

$$\mathbf{C} = \mathbf{A} \pm \mathbf{B} \Leftrightarrow c_{ij} = a_{ij} \pm b_{ij}$$

- Multiplication by a scalar

$$\mathbf{A} = k\mathbf{B} \Leftrightarrow a_{ij} = kb_{ij}$$

Matrix multiplication

- Multiplication by a matrix is defined as

$$\mathbf{C} = \mathbf{A} \bullet \mathbf{B} \Leftrightarrow c_{ij} = \sum_k a_{ik} b_{kj}$$

- Must be commensurate for multiplication
  - Row rank of first must equal column rank of second
- Example

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \begin{bmatrix} 9 & 8 & 7 \\ 6 & 5 & 4 \\ 3 & 2 & 1 \end{bmatrix} = \begin{bmatrix} 30 & 24 & 18 \\ 84 & 69 & 54 \\ 138 & 114 & 90 \end{bmatrix}$$

- Multiplication is not necessarily commutative
  - Order matters

$$\mathbf{A} \bullet \mathbf{B} \neq \mathbf{B} \bullet \mathbf{A}$$

Direct product

- Another kind of matrix multiplication
- Yields an expanded matrix

$$\mathbf{A} \otimes \mathbf{B} = \begin{bmatrix} a_{11}\mathbf{B} & a_{12}\mathbf{B} & \cdots \\ a_{21}\mathbf{B} & a_{22}\mathbf{B} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

- Example direct product

$$\mathbf{A} = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} \quad \mathbf{B} = \begin{bmatrix} 2 & 2 \\ 3 & 1 \end{bmatrix} \Rightarrow \mathbf{A} \otimes \mathbf{B} = \begin{bmatrix} 2 & 2 & 4 & 4 \\ 3 & 1 & 6 & 2 \\ 6 & 6 & 8 & 8 \\ 9 & 3 & 12 & 4 \end{bmatrix}$$

Inverse matrices

- Division of matrices not defined
- Sometimes have the situation

$$\mathbf{A} \bullet \mathbf{B} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbf{1}$$

- **A** is called the left inverse of **B**, and **B** is called the right inverse of **A**
- **1** is known as the identity matrix
  - Analogous to the number 1 in scalar algebra

Orthogonal and unitary matrices

- The relation between a matrix and its inverse specifies its type.
- The inverse of an orthogonal matrix is its transpose.
- The inverse of a unitary matrix is the complex conjugate of its transpose.
- Orthogonal and unitary matrices have identical left and right inverses.

Orthogonal matrix

$$\mathbf{O} \bullet \mathbf{O}^{-1} = \mathbf{1} \quad and \quad \mathbf{O}^{-1} = \mathbf{O}^{\mathrm{T}}$$

Unitary matrix

$$\mathbf{U} \bullet \mathbf{U}^{-1} = \mathbf{1} \quad and \quad \mathbf{U}^{-1} = \left(\mathbf{U}^{\mathrm{T}}\right)^{*}$$

Operations in matrix algebra

- Similarity
  - Two matrices are said to be similar if there exists multiplication by a unitary matrix and it inverse that transforms one into the other

$$\mathbf{A} \xrightarrow{S} \mathbf{B}$$

if

$$\mathbf{B} = \mathbf{U} \bullet \mathbf{A} \bullet \mathbf{U}^{-1}$$

- Real square matrices can be similar to a real diagonal matrix
  - Finding the unitary matrix (and its inverse) is a means of diagonalizing the matrix

$$\mathbf{R} \xrightarrow{S} \mathbf{D}$$

Similarity and eigenvalues

- Similarity to a diagonal matrix allows the determination of matrix eigenvalues
  - Nonzero elements of the diagonal matrix are said to be the eigenvalues of the original matrix
- Diagonalization of a matrix
  - Easily done with computers
  - Gives associated eigenvectors in terms of basis vectors of the matrix

$$\begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix} \xrightarrow{s} \begin{bmatrix} 1 & 0 \\ 0 & 3 \end{bmatrix}$$

Operators

- Many processes in mathematics are thought of as operations.
  - Addition, subtraction, multiplication, division
- Operation is a general term that encompasses other actions.
  - Rotation of a chair
  - Replacement of a letter by a number
  - Removing all vowels from a word to create a new sequence of just consonants
- Every operation has three parts
  - Operator
  - Operand
  - Result

Operator algebra

- Equality $\hat{O}_1 = \hat{O}_2 \Leftrightarrow \left\{ \begin{matrix} \hat{O}_1 f & = & g \\ \hat{O}_2 f & = & g \end{matrix} \right\}$
- Addition
  - Commutativity
  - Distributivity

$$\left(\hat{O}_1 + \hat{O}_2\right) f = \hat{O}_1 f + \hat{O}_2 f$$
$$\hat{O}\left(f + g\right) = \hat{O}f + \hat{O}g$$

- Multiplication
  - Order-sensitive
  - May be noncommutative

$$\left(\hat{O}_1 \bullet \hat{O}_2\right) f = \hat{O}_1\left(\hat{O}_2 f\right)$$
$$\hat{O}_1 \bullet \hat{O}_2 \neq \hat{O}_2 \bullet \hat{O}_1$$

Operators in mathematics

- Operators change functions into other functions

$$\hat{O}\, f(x,y,z) = g(x,y,z)$$

- Example 1: the derivative operator, D

$$\hat{D}\left(x^2 + x + 2\right) = 2x + 1$$

- Example 2: the translation operator, T_h

$$\hat{T}_h\left(x^2 + x + 2\right) = (x+h)^2 + (x+h) + 2$$
$$= x^2 + (2h+1)x + h^2 + h + 2$$

Commutators of operators

- Must establish relations between operators
- One relationship – commutativity
  - Defined by commutator

$$[\hat{A}, \hat{B}]\, f = \hat{A}\left(\hat{B}f\right) - \hat{B}\left(\hat{A}f\right)$$

- Example:

$$[\hat{x}, \hat{x}] = 0$$
$$[\hat{x}, \frac{d}{dx}] = -1$$

Operators and eigenfunctions

- Some operations on some functions give the following special result

$$\hat{O}\, f(x,y,z) = k\, f(x,y,z)$$

- Functions with this property are said to be eigenfunctions of the operator
- The constant *k* is the eigenvalue associated with the eigenfunction
- This is called an eigenvalue equation
- If *O* contains derivative operators, the eigenvalue equation is a differential equation

$$\frac{d}{dx} f_k = k\, f_k$$

Eigenvalue equations in physics

- Represent measurable parameters in quantum mechanics with operators
- Represent possible values with eigenvalues
- Energy -- Schroedinger's equation (contains the Hamiltonian operator)
- Momentum (contains the momentum operator)
- The complete set of eigenfunctions of an operator and the associated eigenvalues represent all possible states of the system.

$$\hat{H}\Psi_k = E_k\Psi_k$$

$$\hat{p}\psi_k = p_k\psi_k$$

Operators for physical variables

- The correspondence principle
  - An operator for a physical parameter is found by substitution into the classical expression
    - For **r** (position), multiplication by **r**
    - For **p** (momentum), the operator is $-i\hbar\nabla$
- The energy operator (the Hamiltonian)

$$H = KE + PE = \frac{p^2}{2m} + V(\mathbf{r}) \Rightarrow \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

Matrix eigenvalue equation

- Matrix equation equivalent to Schroedinger's equation

$$\mathbf{Hc} = \mathbf{Ec}$$

- Diagonalization of **H** gives the eigenvalues and associated eigenvectors
  - The components of **c** for each eigenvalue give the associated eigenvector in terms of the basis vectors relative to which the matrix was defined

Summary

- Matrices are ordered arrays whose algebra is useful in quantum mechanics
  - Algebraic properties are somewhat different from scalar algebra, e.g. matrix multiplication may not be commutative
- Operators are another mathematical device whose algebra is useful in quantum mechanics
  - Correspondence to properties of a physical system
  - Operations may not commute
- Eigenvalue equations
  - Define functions that have a special relation to a particular operator
  - Eigenfunctions are associated with specific constants, eigenvalues
  - Schroedinger's equation is associated with finding quantum states of constant energy