MATHEMATICAL METHODS IN CHEMISTRY

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Mathematical Methods in Chemistry

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About this Book

This text does not replace the calculus courses you take in the mathematics department. In fact, all calculus courses are either a pre- or a co-requisite for this course. Why, then, do student often require Math Methods in Chemistry in their formal chemistry curriculum?

Most students perceive advanced physical chemistry courses, as the most challenging classes they have to take as chemistry majors. Physical chemistry professors will tell you that often, the main problem is that students do not have the mathematical background needed to succeed in the course. How is this possible after all the math you took in your freshman and sophomore years? Even when the mathematics department does a great job at teaching their courses, most chemistry majors have a hard time understanding how to apply the concepts they learned to the problems in chemistry where these concepts are needed. Even students that got all As in their calculus courses freeze when having to use the properties of partial derivatives to derive an equation and they do not remember how to perform a triple integral when required to do so in physical chemistry. At the end of the day, physical chemistry professors end up spending a lot of their time reviewing material they think students should know, and cannot advance with the new material at the level they believe a chemistry major should be at.

This situation is universal, and in fact physical chemistry professors all around the world share the same experiences. The author's chemistry department decided to try an experiment that ended up being a required course in your curriculum. Our philosophy is that if we talk about math directly in the context of chemistry, students will acquire the confidence they need to use math any time they need it. Some of the concepts we will cover in this text are just a refresher of concepts you already saw in your calculus courses. Still, seeing them applied to chemistry will help you understand them deeper than you did when taking calculus. In addition, some students tend to shut down when they feel they are learning something that does not apply to their major, and this (unfortunately!) happens with math all the time. Hopefully, seeing things again in context will motivate you to re-learn the concepts you thought were useless for you. Of course, not everything will be a review. We will learn about linear algebra, differential equations, operators, and other mathematical tools that will be new for most of you. Our goal is that you become comfortable using these tools, and understand why they are important in chemistry. This will be at the cost of not being comprehensive as a mathematics class might be, but this is the penalty we will have to pay for having to survey so much material in one semester. In any case, our hope is that once you feel more confident in your ability to do math, you will be able to continue learning on your own or in other courses as your career takes you through different paths.

Preface

What is Physical Chemistry?

Physical chemistry is the branch of chemistry that aims to develop a fundamental understanding of chemical processes and chemical compounds at the molecular and atomic level. Physical chemistry can be applied to practically any other branch of chemistry, including inorganic chemistry, organic chemistry, atmospheric chemistry, and biochemistry. Modern research in physical chemistry spans topics as varied as environmental and atmospheric processes, the kinetics and dynamics of chemical reactions, the behavior of excited states and their reactivity, the properties of glasses, polymers, liquids and solutions, the physical properties of biomolecules, biomaterials, surfactants and membranes, the principles of energy conversion and storage, etc. Regardless of the application, physical chemists seek to understand chemical systems in quantitative terms.

The need for a strong mathematical foundation

Physical chemistry is the most mathematics-intensive course you will take as a chemistry student. Yet, it would be a mistake to think that only physical chemists need a strong mathematical foundation. Today, more than ever, a strong quantitative foundation is a requisite, or at least a huge advantage, to do research in practically any branch of chemistry. We are well past the days when organic chemistry was built on intuition and good laboratory skills. Today, chemists use mathematical and physical tools to predict the properties of chemicals, the path of reactions, and to design materials with a particular set of properties. Pharmaceutical companies hire chemists to use computational tools that rely heavily on physics and math to predict the interactions between potential drugs and their targets, so they can concentrate on synthesizing only the ones that show some promise. Biochemists can now measure the simultaneous expression levels of tens of thousands of genes in DNA arrays, which produce vast amounts of data that need to be analyzed using mathematical tools. We can find examples of how mathematics plays a central role in almost any field of modern chemistry. **In the 21st century, not having a strong mathematical foundation is a handicap that you cannot afford to have.**

CHAPTER OVERVIEW

1: Before We Begin...

1.1: Things to review

This course requires that you are comfortable with same basic mathematical operations and basic calculus. It is imperative that you go over this chapter carefully and identify the topics you may need to review before starting the semester. You will be too busy learning new concepts soon, so this is the right time for you to seek help if you need it.

Notice: This chapter does not contain a review of topics you should already know. Instead, it gives you a list of topics that you should be comfortable with so you can review them independently if needed. Also, remember that you can use the formula sheet at all times, so locate the information you have and use it whenever needed!

1.1.1 The Equation of a straight line

- given two points calculate the slope, the x-intercept and the y-intercept of the straight line through the points.
- given a graph of a straight line write its corresponding equation.
- given the equation of a straight line sketch the corresponding graph.

1.1.2 Trigonometric Functions

- definition of sin, cos,tan of an angle.
- values of the above trigonometric functions evaluated at 0, $\pi/2$, π, $3/2\pi$, 2π.
- derivatives and primitives of sin and cos.

1.1.3 Logarithms

- the natural logarithm (*[Math Processing Error]*) and its relationship with the exponential function.
- the decimal logarithm (*[Math Processing Error]*) and its relationship with the function *[Math Processing Error]*.
- properties of logarithms (natural and decimal)
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*

1.1.4 The exponential function

- properties
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*
    - *[Math Processing Error]*

1.1.5 Derivatives

- concept of the derivative of a function in terms of the slope of the tangent line.
- derivative of a constant, *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*.
- derivative of the sum of two functions.
- derivative of the product of two functions.
- the chain rule.
- higher derivatives (second, third, etc).
- locating maxima, minima and inflection points.

1.1.6 Indefinite Integrals (Primitives)

- primitive of a constant, *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*.

1.1.7 Definite Integrals

- using limits of integration.
- properties of definite integrals (see recommended exercises below).

Test yourself!

Identify what you need to review by taking this non-graded quiz. http://tinyurl.com/laq5aza

---

1.2: Odd and Even Functions

Many of you probably heard about odd and even functions in previous courses, but for those who did not, here is a brief introduction.

- An odd function obeys the relation *[Math Processing Error]*. For example, *[Math Processing Error]* is odd because *[Math Processing Error]*.
- An even function obeys the relation *[Math Processing Error]*. For example, *[Math Processing Error]* is even because *[Math Processing Error]*.

Even functions are symmetric with respect to the y−axis. In other words, if you were to put a mirror perpendicular to the screen at *[Math Processing Error]*, the right side of the plot would produce a reflection that would overlap with the left side of the plot. Check Figure *[Math Processing Error]* to be sure you understand what this means.

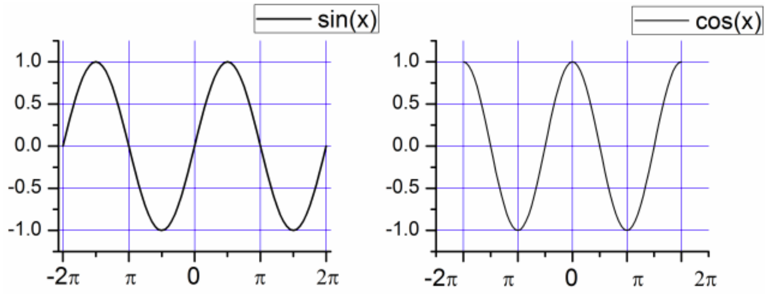

Figure *[Math Processing Error]*: Odd and even functions. (CC BY-NC-SA; Marcia Levitus)

Odd functions are symmetric in a different way. Imagine that you have an axis perpendicular to the screen that contains the point (0,0). Now rotate every point of your graph 180 degrees. If the plot you create after rotation overlaps with the plot before the rotation, the function is odd. Check Figure *[Math Processing Error]* to be sure you understand what this means.

Note that functions do not necessarily need to be even or odd. The function *[Math Processing Error]*, for instance, is clearly neither, as *[Math Processing Error]* (condition for even) and *[Math Processing Error]* (condition for odd). You can also sketch the function *[Math Processing Error]* and verify that it does not have the symmetry of an odd or even function. For any function,

[Math Processing Error]

For an odd function, this integral equals zero:

[Math Processing Error]

This should be obvious just by looking at the plot of *[Math Processing Error]*. The area under the curve between 0 and *[Math Processing Error]* cancels out with the area under the curve between *[Math Processing Error]* and 0. This is great news because it means that we do not have to bother integrating odd functions as long as the limits of integration span from *[Math Processing Error]* to *[Math Processing Error]*, where a can be any number, including infinity. As it turns out this happens often in quantum mechanics, so it is something worth keeping in mind!

For an even function,

[Math Processing Error]

because the area under the curve between 0 and *[Math Processing Error]* equals the area under the curve between *[Math Processing Error]* and 0. This not as helpful as Equation *[Math Processing Error]*, but still might help in some cases. For example, let's say that you need to evaluate *[Math Processing Error]* and the only material that you have available is the formula sheet. You find an expression for

[Math Processing Error]

which you can use with *[Math Processing Error]* to obtain

[Math Processing Error] (be sure you can get this result on your own).

How do you get *[Math Processing Error]*? If the integrand is even, you just need to multiply by 2. This is in fact an even function, because *[Math Processing Error]*, and therefore it is clear that *[Math Processing Error]*. Therefore,

[Math Processing Error]

It is useful to know that the product of two even functions or two odd functions is an even function, and the product of an odd function and an even function is odd. For example,

- *[Math Processing Error]* is the product of two odd functions, and is therefore even.
- *[Math Processing Error]* is the product of two even functions, and is therefore even.
- *[Math Processing Error]* is the product of an odd function and an even function, and is therefore odd.

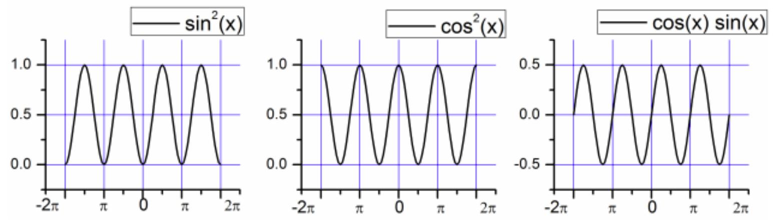

Figure *[Math Processing Error]*: Products of odd and even functions. (CC BY-NC-SA; Marcia Levitus)

> Need help understanding how to identify odd and even functions? External links:
>
> http://www.youtube.com/watch?v=8VgmBe3ulb8
>
> http://www.youtube.com/watch?v=68enNRhFORc

> **Odd, even or neither?**
>
> See if you can classify the functions shown in this short quiz.
>
> http://tinyurl.com/l4pehb8

1.3: The Exponential Function

In Section 1.1 you were asked to review some properties of the exponential function. Here, we will learn (or review) how to sketch exponential functions with negative exponents quickly. These types of functions appear very often in chemistry, so it is important that you know how to visualize them without the help of a computer or calculator.

Suppose we want to sketch the function *[Math Processing Error]*, where *[Math Processing Error]* and *[Math Processing Error]* are positive real numbers (e.g. *[Math Processing Error]*). We could consider negative values of the variable *[Math Processing Error]*, but often *[Math Processing Error]* represents a time or another variable for which only positive values make sense, so we will consider values of *[Math Processing Error]*.

First, let's find out the value of *[Math Processing Error]*, where the function crosses the *[Math Processing Error]*−axis. Because *[Math Processing Error]*, *[Math Processing Error]*. The number *[Math Processing Error]* is often called "the pre-exponential factor" (i.e. the factor before the exponential), or the "amplitude" of the function. This is the amplitude because it will be the highest point in our plot.

Now, let's see what happens as *[Math Processing Error]*. From Section 1.1, it is expected that you know that *[Math Processing Error]*, and therefore, you should be able to conclude that *[Math Processing Error]* decreases from an initial value *[Math Processing Error]* to zero. Whether the function will decay to zero slowly or rapidly will depend on the value of *[Math Processing Error]*.

Let's now consider two points in the curve *[Math Processing Error]*

[Math Processing Error]

and let's further assume that *[Math Processing Error]* (see Figure *[Math Processing Error]*, left). What is the separation between *[Math Processing Error]* and *[Math Processing Error]* *[Math Processing Error]*?

We know that *[Math Processing Error]*, so

[Math Processing Error]

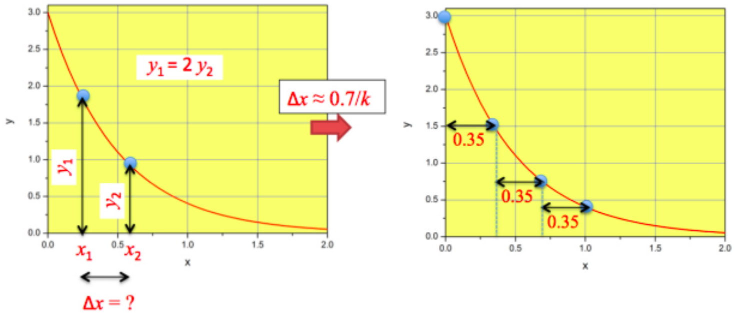

Figure *[Math Processing Error]*: Sketching the function *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

Using the properties of the exponential function:

[Math Processing Error]

and solving for *[Math Processing Error]*:

[Math Processing Error]

This means that the function decays to 50% of its former value every time we move *[Math Processing Error]* units to the right in the *[Math Processing Error]*−axis.

To sketch the function, we just need to remember that *[Math Processing Error]*. Therefore, to sketch *[Math Processing Error]*, we place the first point at *[Math Processing Error]* and *[Math Processing Error]*, and the second point at *[Math Processing Error]* and *[Math Processing Error]*. We can continue adding points following the same logic: every time we drop the value of *[Math Processing Error]* by half, we move *[Math Processing Error]* units to the right in the *[Math Processing Error]*−axis (see Figure *[Math Processing Error]*, right).

> Sketching an exponential function with negative exponent. http://tinyurl.com/n6pdvyh

1.4: The Period of a Periodic Function

A function *[Math Processing Error]* is said to be periodic with period *[Math Processing Error]* if *[Math Processing Error]*. In plain English, the function repeats itself in regular intervals of length *[Math Processing Error]*. The period of the function of Figure *[Math Processing Error]* is *[Math Processing Error]*.

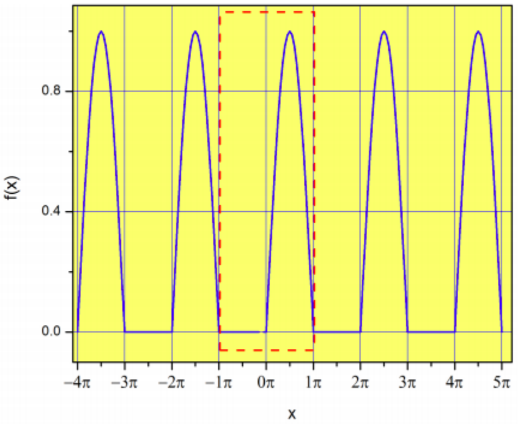

Figure *[Math Processing Error]*: A periodic function with period *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

We know that the period of *[Math Processing Error]* is *[Math Processing Error]*, but what is the period of the function *[Math Processing Error]*?

The period of *[Math Processing Error]* is *[Math Processing Error]*, so:

[Math Processing Error]

By definition, for a periodic function of period *[Math Processing Error]*, the function repeats itself if we add *[Math Processing Error]* to *[Math Processing Error]*:

[Math Processing Error]

Comparing the two equations: *[Math Processing Error]*, and therefore *[Math Processing Error]*.

For example, the period of *[Math Processing Error]* is *[Math Processing Error]*, and the period of *[Math Processing Error]* is *[Math Processing Error]* (see Figure *[Math Processing Error]*).

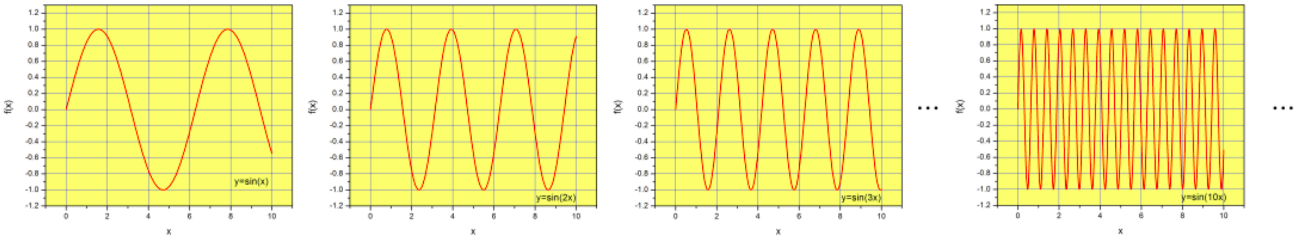

Figure *[Math Processing Error]*: Some examples of the family of functions *[Math Processing Error]*. From left to right: *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

You can follow the same logic to prove that the period of *[Math Processing Error]* is *[Math Processing Error]*. These are important results that we will use later in the semester, so keep them in mind!

> Test yourself with this short quiz! http://tinyurl.com/k4wop6l

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1.5: Exercises

To see if you are on track, solve the following exercises using only the formula sheet (no calculators, computers, books, etc!).

1. Draw the straight line that has a *[Math Processing Error]*-intercept of 3/2 and a slope of 1/2.
2. Express *[Math Processing Error]* as a single fraction.
3. Simplify *[Math Processing Error]*.
4. Express *[Math Processing Error]* as the logarithm of a single number.
5. Given *[Math Processing Error]*, where *[Math Processing Error]*, *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]* are constants, obtain *[Math Processing Error]*
6. Obtain *[Math Processing Error]*
    1. *[Math Processing Error]* (m is a constant).
    2. *[Math Processing Error]*
7. Obtain the first, second and third derivatives of
    1. *[Math Processing Error]*
    2. *[Math Processing Error]*
    3. *[Math Processing Error]*
8. Evaluate *[Math Processing Error]*.
9. Use the properties of integrals and your previous result to evaluate *[Math Processing Error]*. What about *[Math Processing Error]*?
10. Given *[Math Processing Error]* Sketch *[Math Processing Error]* and calculate *[Math Processing Error]*
11. What is the value of this integral? *[Math Processing Error]*
12. Sketch *[Math Processing Error]*. What is the period of the function?
13. The plots below (Figure *[Math Processing Error]*) represent the following functions: *[Math Processing Error]* and *[Math Processing Error]*. Which one is which?

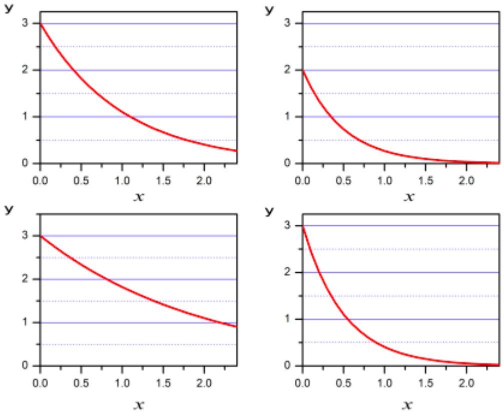

Figure for problem 13. (CC BY-NC-SA; Marcia Levitus)

CHAPTER OVERVIEW

2: Complex Numbers

Chapter Objectives

- Be able to perform basic arithmetic operations with complex numbers.
- Understand the different forms used to express complex numbers (cartesian, polar and complex exponentials).
- Calculate the complex conjugate and the modulus of a number expressed in the different forms (cartesian, polar and complex exponentials).
- Be able to manipulate complex functions.
- Be able to obtain expressions for the complex conjugate and the square of the modulus of a complex function.

2.1: Algebra with Complex Numbers

The imaginary unit *[Math Processing Error]* is defined as the square root of -1: *[Math Processing Error]*. If *[Math Processing Error]* and *[Math Processing Error]* are real numbers, then the number *[Math Processing Error]* is said to be complex. The real number *[Math Processing Error]* is the real part of the complex number *[Math Processing Error]*, and the real number *[Math Processing Error]* is its imaginary part. If *[Math Processing Error]*, then the number is pure imaginary. All the rules of ordinary arithmetic apply with complex numbers, you just need to remember that *[Math Processing Error]* For example, if *[Math Processing Error]* and *[Math Processing Error]*:

- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]* (remember that *[Math Processing Error]*!)
- *[Math Processing Error]*

In order to divide complex numbers we will introduce the concept of complex conjugate.

Complex Conjugate

The complex conjugate of a complex number is defined as the number that has the same real part and an imaginary part which is the negative of the original number. It is usually denoted with a star: If *[Math Processing Error]*, then *[Math Processing Error]*

For example, the complex conjugate of *[Math Processing Error]* is *[Math Processing Error]*. Notice that the product *[Math Processing Error]* is always real:

[Math Processing Error]

We'll use this result in a minute. For now, let's see how the complex conjugate allows us to divide complex numbers with an example:

Example *[Math Processing Error]*: Complex Division

Given *[Math Processing Error]* and *[Math Processing Error]* obtain *[Math Processing Error]*

Solution

[Math Processing Error]

Multiply the numerator and denominator by the complex conjugate of the denominator:

[Math Processing Error]

This "trick" ensures that the denominator is a real number, since *[Math Processing Error]* is always real. In this case,

[Math Processing Error]

The numerator is

[Math Processing Error]

Therefore,

[Math Processing Error]

Example *[Math Processing Error]*

Calculate *[Math Processing Error]* and express your result in cartesian form (*[Math Processing Error]*)

Solution

[Math Processing Error]

The concept of complex conjugate is also useful to calculate the real and imaginary part of a complex number. Given *[Math Processing Error]* and *[Math Processing Error]*, it is easy to see that *[Math Processing Error]* and *[Math Processing Error]*. Therefore:

[Math Processing Error]

and

[Math Processing Error]

You may wonder what is so hard about finding the real and imaginary parts of a complex number by visual inspection. It is certainly not a problem if the number is expressed as *[Math Processing Error]*, but it can be more difficult when dealing with more complicated expressions.

algebra with complex numbers

- Dividing complex numbers: http://tinyurl.com/lkhztm5

External Links:

- Multiplying and dividing complex numbers: http://www.youtube.com/watch?v= KPSj4-76eEc
- Dividing complex numbers: http://www.youtube.com/watch?v=9I4QsSV1XDg

---

2.2: Graphical Representation and Euler Relationship

Complex numbers can be represented graphically as a point in a coordinate plane. In cartesian coordinates, the *[Math Processing Error]*-axis is used for the real part of the number, and the *[Math Processing Error]*-axis is used for the imaginary component. For example, the complex number *[Math Processing Error]* is represented as a point in Figure *[Math Processing Error]*.

Complex numbers can be also represented in polar form. We know that, given a point *[Math Processing Error]* in the plane, *[Math Processing Error]* and *[Math Processing Error]*. Therefore, the complex number *[Math Processing Error]* can be also represented as *[Math Processing Error]*.

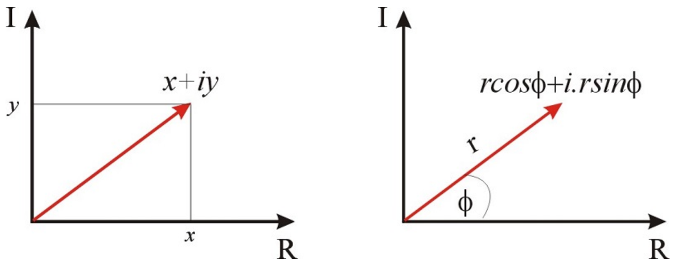

Figure *[Math Processing Error]*: Graphical representation of complex numbers. (CC BY-NC-SA; Marcia Levitus)

We can also represent complex numbers in terms of complex exponentials. This will sound weird for now, but we will see how common and useful this is in physical chemistry as we cover other topics this semester. The Euler relationship relates the trigonometric functions to a complex exponential:

[Math Processing Error]

We will prove this relationship using Taylor series later.

In summary, the complex number *[Math Processing Error]* can be expressed in polar coordinates as *[Math Processing Error]*, and as a complex exponential as *[Math Processing Error]*. The relationships between *[Math Processing Error]* and *[Math Processing Error]* are given by the familiar trigonometric relationships: *[Math Processing Error]* and *[Math Processing Error]*. Notice that

[Math Processing Error]

and

[Math Processing Error]

as we know from Pythagoras' theorem.

✓ Example *[Math Processing Error]*

Express *[Math Processing Error]* in the form *[Math Processing Error]*

Solution

[Math Processing Error] and *[Math Processing Error]*.

We know that

[Math Processing Error] and *[Math Processing Error]*

Dividing *[Math Processing Error]*, we get *[Math Processing Error]*. In this problem *[Math Processing Error]*, and therefore *[Math Processing Error]*.

To obtain *[Math Processing Error]* we use *[Math Processing Error]*. In this case:

[Math Processing Error]

Therefore, *[Math Processing Error]*

From Equation *[Math Processing Error]* we can see how the trigonometric functions can be expressed as complex exponentials:

[Math Processing Error]

Again, this may look strange at this point, but it turns out that exponentials are much easier to manipulate than trigonometric functions (think about multiplying or dividing exponentials vs. trigonometric functions), so it is common that physical chemists write equations in terms of complex exponentials instead of cosines and sines.

In Equation *[Math Processing Error]* we saw that *[Math Processing Error]*. Now we know that this equals *[Math Processing Error]*, where *[Math Processing Error]* is the modulus or absolute value of the vector represented in red in Figure *[Math Processing Error]*. Therefore, the modulus of a complex number, denoted as *[Math Processing Error]*, can be calculated as:

[Math Processing Error]

✓ Example *[Math Processing Error]*

Obtain the modulus of the complex number *[Math Processing Error]* (see Example *[Math Processing Error]*)

Solution

[Math Processing Error]

external links

- Expressing a complex number in polar form I: http://www.youtube.com/watch?v=6z6fzPXUbSQs
- Expressing a complex number in polar form II: http://www.youtube.com/watch?v=tAIxdEVuTZ8
- Expressing a complex number in polar form III: http://www.youtube.com/watch?v=XIYDO_weAVA

2.3: Complex Functions

The concepts of complex conjugate and modulus that we discussed above can also be applied to complex functions. For instance, in quantum mechanics, atomic orbitals are often expressed in terms of complex exponentials. For example, one of the *[Math Processing Error]* orbitals of the hydrogen atom can be expressed in spherical coordinates (*[Math Processing Error]*) as

[Math Processing Error]

We will work with orbitals and discuss their physical meaning throughout the semester. For now, let's write an expression for the square of the modulus of the orbital (Equation *[Math Processing Error]*):

[Math Processing Error]

The complex conjugate of a complex function is created by changing the sign of the imaginary part of the function (in lay terms, every time you see a +*[Math Processing Error]* change it to a -*[Math Processing Error]*, and every time you see a -*[Math Processing Error]* change it to a +*[Math Processing Error]*). Therefore:

[Math Processing Error]

Notice that *[Math Processing Error]* is **always** real because the term

[Math Processing Error]

This has to be the case because *[Math Processing Error]* represents the square of the modulus, and as we will discuss many times during the semester, it can be interpreted in terms of the probability of finding the electron in different regions of space. Because probabilities are physical quantities that are positive, it is good that *[Math Processing Error]* is guaranteed to be real!

> Confused about the complex conjugate? See how to write the complex conjugate in the different notations discussed in this chapter in this short video: http://tinyurl.com/ lcry7ma

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2.4: Problems

Note: Always express angles in radians (e.g. *[Math Processing Error]*, not *[Math Processing Error]*). When expressing complex numbers in Cartesian form always finish your work until you can express them as *[Math Processing Error]*. For example, if you obtain *[Math Processing Error]*, multiply and divide the denominator by its complex conjugate to obtain *[Math Processing Error]*.

Remember: No calculators allowed!

? Problem *[Math Processing Error]*

Given *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*, obtain:

- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*
- Express *[Math Processing Error]* as a complex exponential
- *[Math Processing Error]*
- *[Math Processing Error]*, and express the result in cartesian form
- Display the three numbers in the same plot (real part in the *[Math Processing Error]*-axis and imaginary part in the *[Math Processing Error]*-axis)

? Problem *[Math Processing Error]*

The following family of functions are encountered in quantum mechanics:

[Math Processing Error]

Notice the difference between *[Math Processing Error]* (the name of the function), and *[Math Processing Error]* (the independent variable). The definition above defines a family of functions (one function for each value of *[Math Processing Error]*). For example, for *[Math Processing Error]*:

[Math Processing Error]

and for *[Math Processing Error]*:

[Math Processing Error]

- Obtain *[Math Processing Error]*
- Calculate *[Math Processing Error]*
- Calculate *[Math Processing Error]* for *[Math Processing Error]*
- Calculate *[Math Processing Error]* for *[Math Processing Error]*
- Calculate *[Math Processing Error]* for *[Math Processing Error]*

? Problem *[Math Processing Error]*

Given the function

[Math Processing Error]

Write down an expression for *[Math Processing Error]*

CHAPTER OVERVIEW

3: Series

Chapter Objectives

- Learn how to obtain Maclaurin and Taylor expansions of different functions.
- Learn how to express infinite sums using the summation operator (*[Math Processing Error]*)
- Understand how a series expansion can be used in the physical sciences to obtain an approximation that is valid in a particular regime (e.g. low concentration of solute, low pressure of a gas, small oscillations of a pendulum, etc).
- Understand how a series expansion can be used to prove a mathematical relationship.

3.1: Maclaurin Series

A function *[Math Processing Error]* can be expressed as a series in powers of *[Math Processing Error]* as long as *[Math Processing Error]* and all its derivatives are finite at *[Math Processing Error]*. For example, we will prove shortly that the function *[Math Processing Error]* can be expressed as the following infinite sum:

[Math Processing Error]

We can write this statement in this more elegant way:

[Math Processing Error]

If you are not familiar with this notation, the right side of the equation reads "sum from *[Math Processing Error]* to *[Math Processing Error]* of *[Math Processing Error]*" When *[Math Processing Error]*, *[Math Processing Error]*, when *[Math Processing Error]*, *[Math Processing Error]*, when *[Math Processing Error]*, *[Math Processing Error]*, etc (compare with Equation *[Math Processing Error]*). The term "series in powers of *[Math Processing Error]*" means a sum in which each summand is a power of the variable *[Math Processing Error]*. Note that the number 1 is a power of *[Math Processing Error]* as well (*[Math Processing Error]*). Also, note that both Equations *[Math Processing Error]* and *[Math Processing Error]* are exact, they are not approximations.

Similarly, we will see shortly that the function *[Math Processing Error]* can be expressed as another infinite sum in powers of *[Math Processing Error]* (i.e. a Maclaurin series) as:

[Math Processing Error]

Or, more elegantly:

[Math Processing Error]

where *[Math Processing Error]* is read "n factorial" and represents the product *[Math Processing Error]*. If you are not familiar with factorials, be sure you understand why *[Math Processing Error]*. Also, remember that by definition *[Math Processing Error]*, not zero.

At this point you should have two questions: 1) how do I construct the Maclaurin series of a given function, and 2) why on earth would I want to do this if *[Math Processing Error]* and *[Math Processing Error]* are fine-looking functions as they are. The answer to the first question is easy, and although you should know this from your calculus classes we will review it again in a moment. The answer to the second question is trickier, and it is what most students find confusing about this topic. We will discuss different examples that aim to show a variety of situations in which expressing functions in this way is helpful.

How to obtain the Maclaurin Series of a Function

In general, a well-behaved function (*[Math Processing Error]* and all its derivatives are finite at *[Math Processing Error]*) will be expressed as an infinite sum of powers of *[Math Processing Error]* like this:

[Math Processing Error]

Be sure you understand why the two expressions in Equation *[Math Processing Error]* are identical ways of expressing an infinite sum. The terms *[Math Processing Error]* are called the **coefficients**, and are constants (that is, they are NOT functions of *[Math Processing Error]*). If you end up with the variable *[Math Processing Error]* in one of your coefficients go back and check what you did wrong! For example, in the case of *[Math Processing Error]* (Equation *[Math Processing Error]*), *[Math Processing Error]*. In the example of Equation *[Math Processing Error]*, all the coefficients equal 1. We just saw that two very different functions can be expressed using the same set of functions (the powers of *[Math Processing Error]*). What makes *[Math Processing Error]* different from *[Math Processing Error]* are the coefficients *[Math Processing Error]*. As we will see shortly, the coefficients can be negative, positive, or zero.

How do we calculate the coefficients? Each coefficient is calculated as:

[Math Processing Error]

That is, the *[Math Processing Error]*-th coefficient equals one over the factorial of *[Math Processing Error]* multiplied by the *[Math Processing Error]*-th derivative of the function *[Math Processing Error]* evaluated at zero. For example, if we want to calculate *[Math Processing Error]* for the function *[Math Processing Error]*, we need to get the second derivative of *[Math*

Processing Error], evaluate it at *[Math Processing Error]*, and divide the result by *[Math Processing Error]*. Do it yourself and verify that *[Math Processing Error]*. In the case of *[Math Processing Error]* we need the zeroth-order derivative, which equals the function itself (that is, *[Math Processing Error]*, because *[Math Processing Error]*). It is important to stress that although the derivatives are usually functions of *[Math Processing Error]*, the coefficients are constants because they are expressed in terms of the derivatives evaluated at *[Math Processing Error]*.

Note that in order to obtain a Maclaurin series we evaluate the function and its derivatives at *[Math Processing Error]*. This procedure is also called the expansion of the function around (or about) zero. We can expand functions around other numbers, and these series are called Taylor series (see Section 3).

✓ Example *[Math Processing Error]*

Obtain the Maclaurin series of *[Math Processing Error]*.

Solution

We need to obtain all the coefficients (*[Math Processing Error]*). Because there are infinitely many coefficients, we will calculate a few and we will find a general pattern to express the rest. We will need several derivatives of *[Math Processing Error]*, so let's make a table:

[Math Processing Error]	***[Math Processing Error]***	***[Math Processing Error]***
0	*[Math Processing Error]*	0
1	*[Math Processing Error]*	1
2	*[Math Processing Error]*	0
3	*[Math Processing Error]*	-1
4	*[Math Processing Error]*	0
5	*[Math Processing Error]*	1

Remember that each coefficient equals *[Math Processing Error]* divided by *[Math Processing Error]*, therefore:

[Math Processing Error]	***[Math Processing Error]***	***[Math Processing Error]***
0	1	0
1	1	1
2	2	0
3	*[Math Processing Error]*	*[Math Processing Error]*
4	*[Math Processing Error]*	0
5	*[Math Processing Error]*	*[Math Processing Error]*

This is enough information to see the pattern (you can go to higher values of *[Math Processing Error]* if you don't see it yet):

1. the coefficients for even values of *[Math Processing Error]* equal zero.
2. the coefficients for *[Math Processing Error]* equal *[Math Processing Error]*
3. the coefficients for *[Math Processing Error]* equal *[Math Processing Error]*.

Recall that the general expression for a Maclaurin series is *[Math Processing Error]*, and replace *[Math Processing Error]* by the coefficients we just found:

[Math Processing Error]

This is a correct way of writing the series, but in the next example we will see how to write it more elegantly as a sum.

✓ Example *[Math Processing Error]*

Express the Maclaurin series of *[Math Processing Error]* as a sum.

Solution

In the previous example we found that:

[Math Processing Error]

We want to express this as a sum:

[Math Processing Error]

The key here is to express the coefficients *[Math Processing Error]* in terms of *[Math Processing Error]*. We just concluded that 1) the coefficients for even values of *[Math Processing Error]* equal zero, 2) the coefficients for *[Math Processing Error]* equal *[Math Processing Error]* and 3) the coefficients for *[Math Processing Error]* equal *[Math Processing Error]*. How do we put all this information together in a unique expression? Here are three possible (and equally good) answers:

- *[Math Processing Error]*
- *[Math Processing Error]*
- *[Math Processing Error]*

This may look impossibly hard to figure out, but let me share a few tricks with you. First, we notice that the sign in Equation *[Math Processing Error]* alternates, starting with a "+". A mathematical way of doing this is with a term *[Math Processing Error]* if your sum starts with *[Math Processing Error]*, or *[Math Processing Error]* if you sum starts with *[Math Processing Error]*. Note that *[Math Processing Error]* does the same trick.

[Math Processing Error]	***[Math Processing Error]***	***[Math Processing Error]***	***[Math Processing Error]***
0	1	-1	1
1	-1	1	-1
2	1	-1	1
3	-1	1	-1

We have the correct sign for each term, but we need to generate the numbers *[Math Processing Error]* Notice that the number "1" can be expressed as *[Math Processing Error]*. To do this, we introduce the second trick of the day: we will use the expression *[Math Processing Error]* to generate odd numbers (if you start your sum with *[Math Processing Error]*) or *[Math Processing Error]* (if you start at *[Math Processing Error]*). Therefore, the expression *[Math Processing Error]* gives *[Math Processing Error]*, which is what we need in the first and third examples (when the sum starts at zero).

Lastly, we need to use only odd powers of *[Math Processing Error]*. The expression *[Math Processing Error]* generates the terms *[Math Processing Error]* when you start at *[Math Processing Error]*, and *[Math Processing Error]* achieves the same when you start your series at *[Math Processing Error]*.

Confused about writing sums using the sum operator *[Math Processing Error]*? This video will help: http://tinyurl.com/lvwd36q

Need help? The links below contain solved examples.

External links:

Finding the maclaurin series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-1/

Finding the maclaurin series of a function II: http://www.youtube.com/watch?v= dp2ovDuWhro

Finding the maclaurin series of a function III: http://www.youtube.com/watch?v= WWe7pZjc4s8

Graphical Representation

From Equation *[Math Processing Error]* and the examples we discussed above, it should be clear at this point that any function whose derivatives are finite at *[Math Processing Error]* can be expressed by using the same set of functions: the powers of *[Math Processing Error]*. We will call these functions the **basis set**. A basis set is a collection of linearly independent functions that can represent other functions when used in a linear combination.

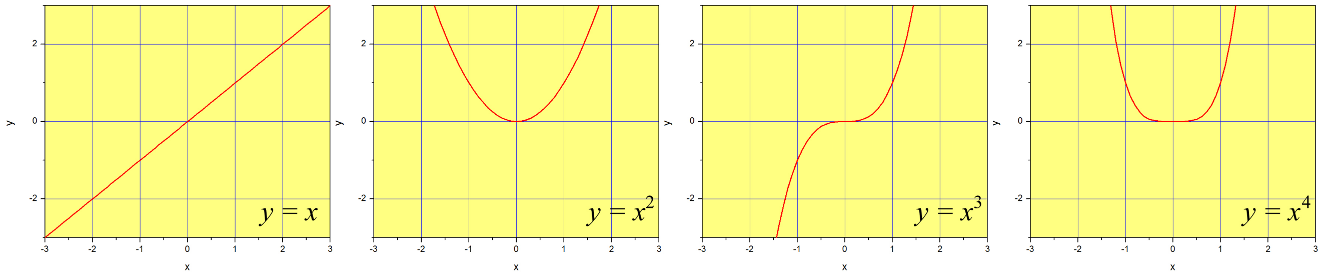


Figure *[Math Processing Error]*: Some of the functions of the basis set for a Maclaurin expansion (CC BY-NC-SA; Marcia Levitus)

Figure *[Math Processing Error]* is a graphic representation of the first four functions of this basis set. To be fair, the first function of the set is *[Math Processing Error]*, so these would be the second, third, fourth and fifth. The full basis set is of course infinite in length. If we mix all the functions of the set with equal weights (we put the same amount of *[Math Processing Error]* than we put *[Math Processing Error]* or *[Math Processing Error]*), we obtain *[Math Processing Error]* (Equation *[Math Processing Error]*. If we use only the odd terms, alternate the sign starting with a '+', and weigh each term less and less using the expression *[Math Processing Error]* for the *[Math Processing Error]* term, we obtain *[Math Processing Error]* (Equation *[Math Processing Error]*). This is illustrated in Figure *[Math Processing Error]*, where we multiply the even powers of *[Math Processing Error]* by zero, and use different weights for the rest. Note that the 'etcetera' is crucial, as we would need to include an infinite number of functions to obtain the function *[Math Processing Error]* exactly.

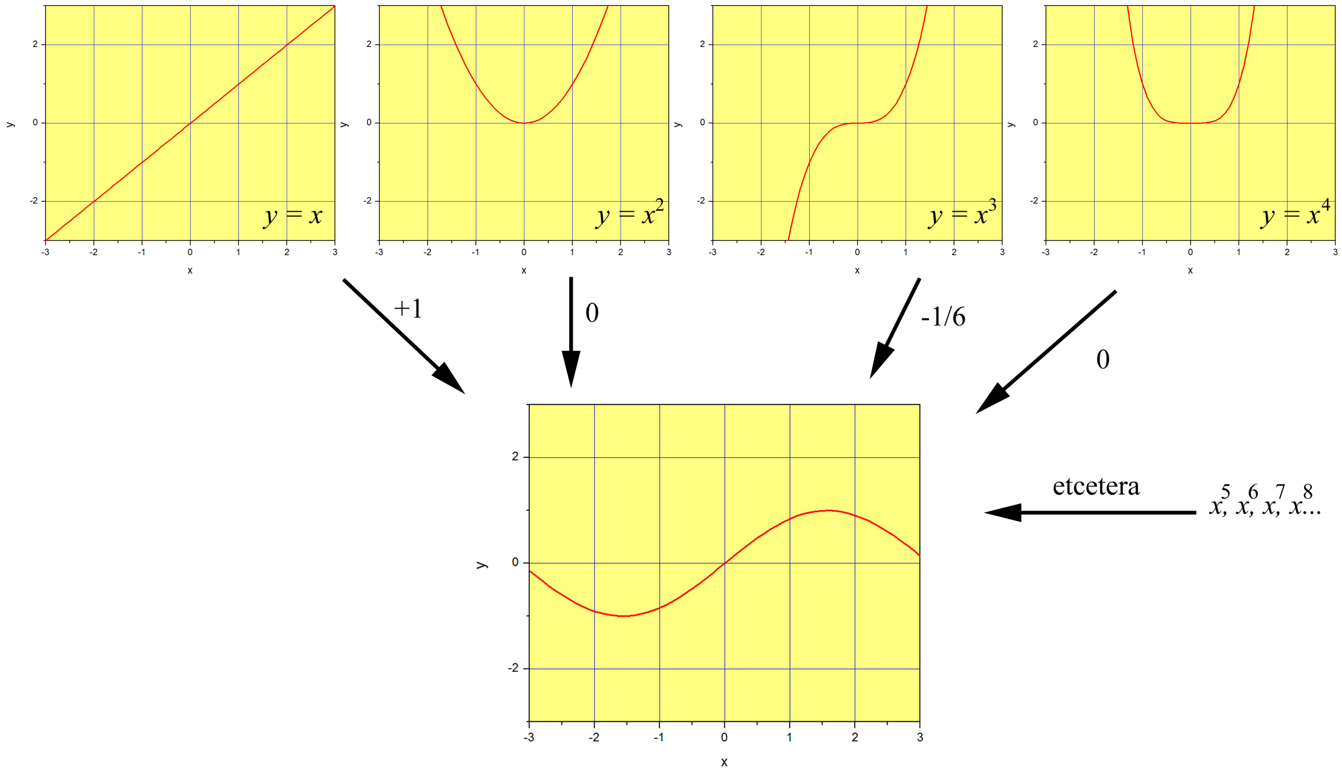


Figure *[Math Processing Error]*: Construction of *[Math Processing Error]* using the powers of *[Math Processing Error]* as the basis set. (CC BY-NC-SA; Marcia Levitus)

Although we need an infinite number of terms to express a function exactly (unless the function is a polynomial, of course), in many cases we will observe that the weight (the coefficient) of each power of *[Math Processing Error]* gets smaller and smaller as we increase the power. For example, in the case of *[Math Processing Error]*, the contribution of *[Math Processing Error]* is *[Math Processing Error]* of the contribution of *[Math Processing Error]* (in absolute terms), and the contribution of *[Math Processing Error]* is *[Math Processing Error]*. This tells you that the first terms are much more important than the rest, although all are needed if we want the sum to represent *[Math Processing Error]* exactly. What if we are happy with a ‘pretty good’ approximation of *[Math Processing Error]*? Let’s see what happens if we use up to *[Math Processing Error]* and drop the higher terms. The result is plotted in blue in Figure *[Math Processing Error]* together with *[Math Processing Error]* in red. We can see that the function *[Math Processing Error]* is a very good approximation of *[Math Processing Error]* as long as we stay close to *[Math Processing Error]*. As we move further away from the origin the approximation gets worse and worse, and we would need to include higher powers of *[Math Processing Error]* to get it better. This should be clear from eq. [series:sin], since the terms *[Math Processing Error]* get smaller and smaller with increasing *[Math Processing Error]* if *[Math Processing Error]* is a small number. Therefore, if *[Math Processing Error]* is small, we could write *[Math Processing Error]*, where the symbol *[Math Processing Error]* means approximately equal.

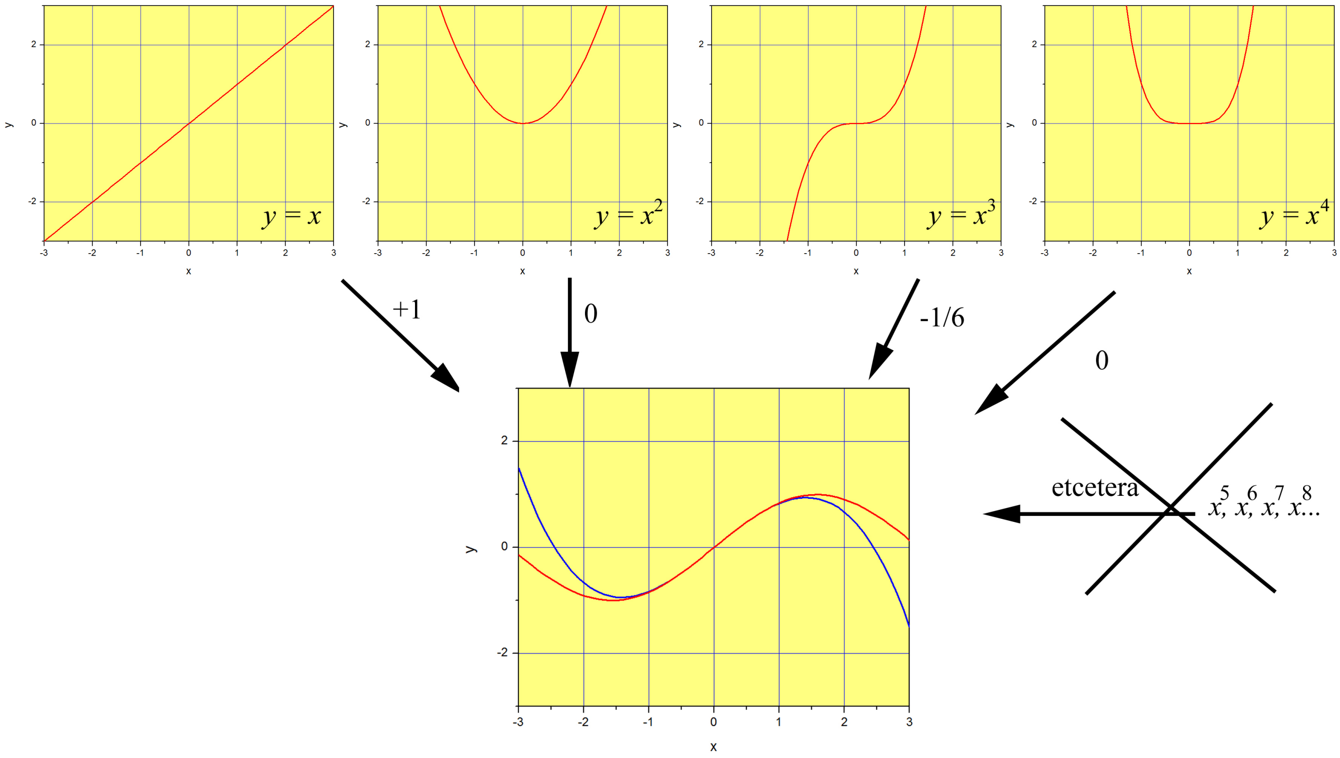


Figure *[Math Processing Error]*: Approximation of *[Math Processing Error]* up to the third power of *[Math Processing Error]*. The curve in blue is the function *[Math Processing Error]*, and the curve in red is *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

But why stopping at *[Math Processing Error]* and not *[Math Processing Error]* or 5? The above argument suggests that the function *[Math Processing Error]* might be a good approximation of *[Math Processing Error]* around *[Math Processing Error]*, when the term *[Math Processing Error]* is much smaller than the term *[Math Processing Error]*. This is in fact this is the case, as shown in Figure *[Math Processing Error]*.

We have seen that we can get good approximations of a function by **truncating** the series (i.e. not using the infinite terms). Students usually get frustrated and want to know how many terms are ‘correct’. It takes a little bit of practice to realize there is no universal answer to this question. We would need some context to analyze how good of an approximation we are happy with. For example, are we satisfied with the small error we see at *[Math Processing Error]* in Figure *[Math Processing Error]*? It all depends on the context. Maybe we are performing experiments where we have other sources of error that are much worse than this, so using an extra term will not improve the overall situation anyway. Maybe we are performing very precise experiments where this difference is significant. As you see, discussing how many terms are needed in an approximation out of context is not very useful.

We will discuss this particular approximation when we learn about second order differential equations and analyze the problem of the pendulum, so hopefully things will make more sense then.

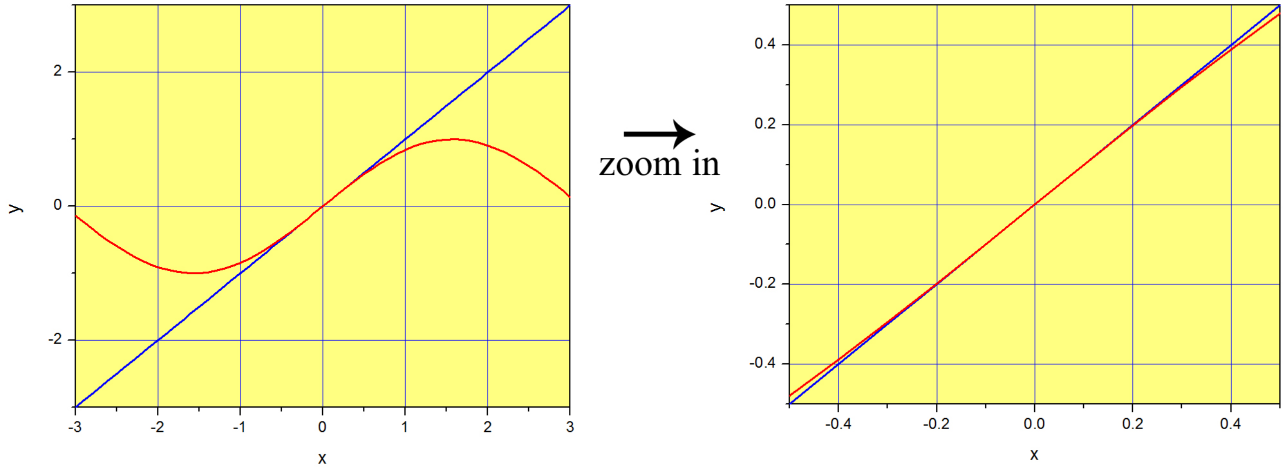


Figure *[Math Processing Error]*: Approximation of *[Math Processing Error]* up to the first power of *[Math Processing Error]*. The curve in blue is the function *[Math Processing Error]*, and the curve in red is *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

3.2: Linear Approximations

If you take a look at Equation $3.1.5$ you will see that we can always approximate a function as $a_0 + a_1 x$ as long as x is small. When we say 'any function' we of course imply that the function and all its derivatives need to be finite at $x = 0$. Looking at the definitions of the coefficients, we can write:

$$f(x) \approx f(0) + f'(0)x \tag{3.2.1}$$

We call this a linear approximation because Equation 3.2.1 is the equation of a straight line. The slope of this line is $f'(0)$ and the y-intercept is $f(0)$.

A fair question at this point is 'why are we even talking about approximations?' What is so complicated about the functions $\sin x$, e^x or $\ln(x+1)$ that we need to look for an approximation? Are we getting too lazy? To illustrate this issue, let's consider the problem of the pendulum, which we will solve in detail in the chapter devoted to differential equations. The problem is illustrated in Figure $3.2.1$, and those of you who took a physics course will recognize the equation below, which represents the law of motion of a simple pendulum. The second derivative refers to the acceleration, and the $\sin\theta$ term is due to the component of the net force along the direction of motion. We will discuss this in more detail later in this semester, so for now just accept the fact that, for this system, Newton's law can be written as:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\sin\theta(t) = 0$$

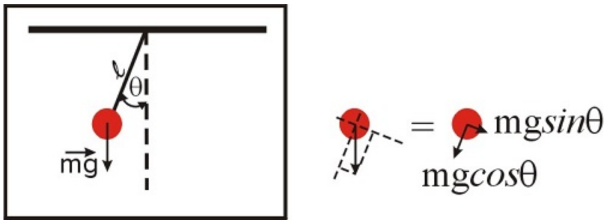


Figure $3.2.1$: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

This equation should be easy to solve, right? It has only a few terms, nothing too fancy other than an innocent sine function...How difficult can it be to obtain $\theta(t)$? Unfortunately, this differential equation does not have an analytical solution! An analytical solution means that the solution can be expressed in terms of a finite number of elementary functions (such as sine, cosine, exponentials, etc). Differential equations are sometimes deceiving in this way: they look simple, but they might be incredibly hard to solve, or even impossible! The fact that we cannot write down an analytical solution does not mean there is no solution to the problem. You can swing a pendulum and measure $\theta(t)$ and create a table of numbers, and in principle you can be as precise as you want to be. Yet, you will not be able to create a function that reflects your numeric results. We will see that we can solve equations like this numerically, but not analytically. Disappointing, isn't it? Well... don't be. A lot of what we know about molecules and chemical reactions came from the work of physical chemists, who know how to solve problems using numerical methods. The fact that we cannot obtain an analytical expression that describes a particular physical or chemical system does not mean we cannot solve the problem numerically and learn a lot anyway!

But what if we are interested in small displacements only (that is, the pendulum swings close to the vertical axis at all times)? In this case, $\theta << 1$, and as we saw $\sin\theta \approx \theta$ (see Figure $3.1.4$). If this is the case, we have now:

$$\frac{d^2\theta(t)}{dt^2} + \frac{g}{l}\theta(t) = 0$$

As it turns out, and as we will see in Chapter 2, in this case it is very easy to obtain the solution we are looking for:

$$\theta(t) = \theta(t=0)\cos\left(\left(\frac{g}{l}\right)^{1/2} t\right)$$

This solution is the familiar 'back and forth' oscillatory motion of the pendulum you are familiar with. What you might have not known until today is that this solution assumes $\sin\theta \approx \theta$ and is therefore valid only if $\theta << 1$!

There are lots of ‘hidden’ linear approximations in the equations you have learned in your physics and chemistry courses. You may recall your teachers telling you that a give equation is valid only at low concentrations, or low pressures, or low... you hopefully get the point. A pendulum is of course not particularly interesting when it comes to chemistry, but as we will see through many examples during the semester, oscillations, generally speaking, are. The example below illustrates the use of series to a problem involving diatomic molecules, but before discussing it we need to provide some background.

The vibrations of a diatomic molecule are often modeled in terms of the so-called *Morse potential*. This equation does not provide an exact description of the vibrations of the molecule under any condition, but it does a pretty good job for many purposes.

$$V(R)=D_e\left(1-e^{-k(R-R_e)}\right)^2 \tag{3.2.2}$$

Here, R is the distance between the nuclei of the two atoms, R_e is the distance at equilibrium (i.e. the equilibrium bond length), D_e is the dissociation energy of the molecule, k is a constant that measures the strength of the bond, and V is the potential energy. Note that R_e is the distance at which the potential energy is a minimum, and that is why we call this the equilibrium distance. We would need to apply energy to separate the atoms even more, or to push them closer (Figure $3.2.2$).

At room temperature, there is enough thermal energy to induce small vibrations that displace the atoms from their equilibrium positions, but for stable molecules, the displacement is very small: $R-R_e\rightarrow 0$. In the next example we will prove that under these conditions, the potential looks like a parabola, or in mathematical terms, $V(R)$ is proportional to the square of the displacement. This type of potential is called a ’harmonic potential’. A vibration is said to be simple harmonic if the potential is proportional to the square of the displacement (as in the simple spring problems you may have studied in physics).

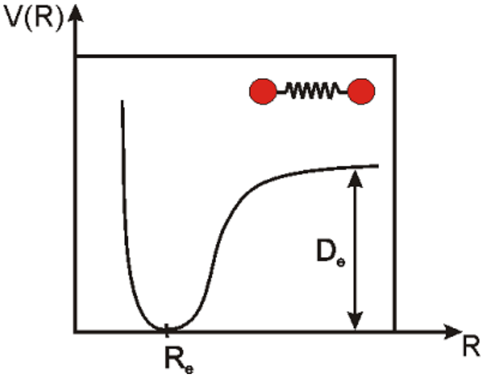


Figure $3.2.2$: The Morse potential (CC BY-NC-SA; Marcia Levitus)

Example $3.2.1$

Expand the Morse potential as a power series and prove that the vibrations of the molecule are approximately simple harmonic if the displacement $R-R_e$ is small.

Solution

The relevant variable in this problem is the displacement $R-R_e$, not the actual distance R. Let’s call the displacement $R-R_e=x$, and let’s rewrite Equation $3.2.2$ as

$$V(R)=D_e\left(1-e^{-kx}\right)^2 \tag{3.2.3}$$

The goal is to prove that $V(R)=cx^2$ (i.e. the potential is proportional to the square of the displacement) when $x\rightarrow 0$. The constant c is the proportionality constant. We can approach this in two different ways. One option is to expand the function shown in Equation $3.2.3$ around zero. This would be correct, but it but involve some unnecessary work. The variable x appears only in the exponential term, so a simpler option is to expand the exponential function, and plug the result of this expansion back in Equation $3.2.3$. Let’s see how this works:

We want to expand e^{-kx} as $a_0+a_1x+a_2x^2...a_nx^n$, and we know that the coefficients are $a_n=\frac{1}{n!}\left(\frac{d^nf(x)}{dx^n}\right)_0$.
The coefficient a_0 is $f(0)=1$. The first three derivatives of $f(x)=e^{-kx}$ are

- $f'(x)=-ke^{-kx}$
- $f''(x)=k^2e^{-kx}$

- $f'''(x) = -k^3 e^{-kx}$

When evaluated at $x = 0$ we obtain, $-k, k^2, -k^3 \dots$

and therefore $a_n = \frac{(-1)^n k^n}{n!}$ for $n = 0, 1, 2 \dots$.

Therefore,

$$e^{-kx} = 1 - kx + k^2x^2/2! - k^3x^3/3! + k^4x^4/4! \dots$$

and

$$1 - e^{-kx} = +kx - k^2x^2/2! + k^3x^3/3! - k^4x^4/4! \dots$$

From the last result, when $x << 1$, we know that the terms in $x^2, x^3 \dots$ will be increasingly smaller, so $1 - e^{-kx} \approx kx$ and $(1 - e^{-kx})^2 \approx k^2x^2$.

Plugging this result in Equation 3.2.3 we obtain $V(R) \approx D_e k^2 x^2$, so we demonstrated that the potential is proportional to the square of the displacement when the displacement is small (the proportionality constant is $D_e k^2$). Therefore, stable diatomic molecules at room temperatures behave pretty much like a spring! (Don't take this too literally. As we will discuss later, microscopic springs do not behave like macroscopic springs at all).

3.3: Taylor Series

Before discussing more applications of Maclaurin series, let's expand our discussion to the more general case where we expand a function around values different from zero. Let's say that we want to expand a function around the number h. If $h=0$, we call the series a Maclaurin series, and if $h\neq 0$ we call the series a Taylor series. Because Maclaurin series are a special case of the more general case, we can call all the series Taylor series and omit the distinction. The following is true for a function $f(x)$ as long as the function and all its derivatives are finite at h:

$$f(x)=a_0+a_1(x-h)+a_2(x-h)^2+\ldots+a_n(x-h)^n=\sum_{n=0}^{\infty}a_n(x-h)^n \tag{3.3.1}$$

The coefficients are calculated as

$$a_n=\frac{1}{n!}\left(\frac{d^nf}{dx^n}\right)_h \tag{3.3.2}$$

Notice that instead of evaluating the function and its derivatives at $x=0$ we now evaluate them at $x=h$, and that the basis set is now $1,(x-h),(x-h)^2,\ldots,(x-h)^n$ instead of $1,x,x^2,\ldots,x^n$. A Taylor series will be a good approximation of the function at values of x close to h, in the same way Maclaurin series provide good approximations close to zero.

To see how this works let's go back to the exponential function. Recall that the Maclaurin expansion of e^x is shown in Equation $3.1.3$. We know what happens if we expand around zero, so to practice, let's expand around $h=1$. The coefficient a_0 is $f(1)=e^1=e$. All the derivatives are e^x, so $f'(1)=f''(1)=f'''(1)\ldots=e.$ Therefore, $a_n=\frac{e}{n!}$ and the series is therefore

$$e\left[1+(x-1)+\frac{1}{2}(x-1)^2+\frac{1}{6}(x-1)^3+\ldots\right]=\sum_{n=0}^{\infty}\frac{e}{n!}(x-1)^n \tag{3.3.3}$$

We can use the same arguments we used before to conclude that $e^x\approx ex$ if $x\approx 1$. If $x\approx 1$, $(x-1)\approx 0$, and the terms $(x-1)^2,(x-1)^3$ will be smaller and smaller and will contribute less and less to the sum. Therefore,

$$e^x\approx e\left[1+(x-1)\right]=ex.$$

This is the equation of a straight line with slope e and y-intercept 0. In fact, from Equation $3.1.7$ we can see that all functions will look linear at values close to h. This is illustrated in Figure $3.3.1$, which shows the exponential function (red) together with the functions $1+x$ (magenta) and ex (blue). Not surprisingly, the function $1+x$ provides a good approximation of e^x at values close to zero (see Equation $3.1.3$) and the function ex provides a good approximation around $x=1$ (Equation 3.3.3).

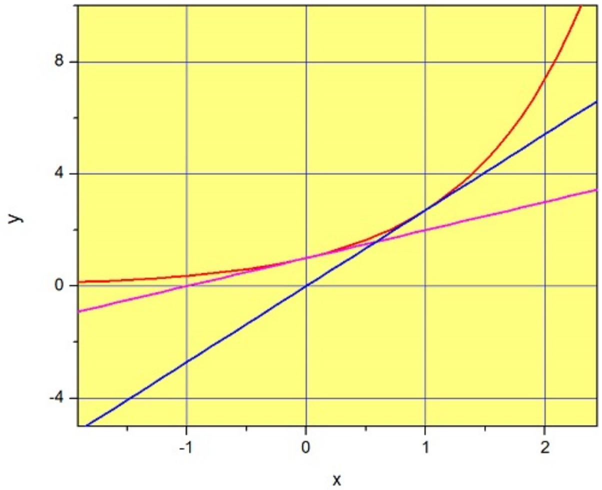


Figure $3.3.1$: Two linear approximations of the exponential function. The function e^x is plotted in red together with the function $y=1+x$ (magenta) and $y=ex$ (blue). (CC BY-NC-SA; Marcia Levitus)

✓ Example 3.3.1:

Expand $f(x)=\ln x$ about $x=1$

Solution

$$f(x)=a_0+a_1(x-h)+a_2(x-h)^2+\ldots+a_n(x-h)^n, a_n=\frac{1}{n!}\left(\frac{d^nf}{dx^n}\right)_h$$

$$a_0=f(1)=\ln(1)=0$$

The derivatives of $\ln x$ are:

$$f'(x)=1/x, f''(x)=-1/x^2, f'''(x)=2/x^3, f^{(4)}(x)=-6/x^4, f^{(5)}(x)=24/x^5\ldots$$

and therefore,

$$f'(1)=1, f''(1)=-1, f'''(1)=2, f^{(4)}(1)=-6, f^{(5)}(1)=24\ldots.$$

To calculate the coefficients, we need to divide by $n!$:

- $a_1=f'(1)/1!=1$
- $a_2=f''(1)/2!=-1/2$
- $a_3=f'''(1)/3!=2/3!=1/3$
- $a_4=f^{(4)}(1)/4!=-6/4!=-1/4$
- $a_n=(-1)^{n+1}/n$

The series is therefore:

$$f(x)=0+1(x-1)-1/2(x-1)^2+1/3(x-1)^3\ldots=\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}(x-1)^n$$

Note that we start the sum at $n=1$ because $a_0=0$, so the term for $n=0$ does not have any contribution.

Need help? The links below contain solved examples.

External links:

Finding the Taylor series of a function I: http://patrickjmt.com/taylor-and-maclaurin-series-example-2/

3.4: Other Applications of Mclaurin and Taylor series

So far we have discussed how we can use power series to approximate more complex functions around a particular value. This is very common in physical chemistry, and you will apply it frequently in future courses. There are other useful applications of Taylor series in the physical sciences. Sometimes, we may use relationships to derive equations or prove relationships. Example *[Math Processing Error]* illustrates this last point.

✓ Example *[Math Processing Error]*

Calculate the following sum (*[Math Processing Error]* is a positive constant)

[Math Processing Error]

Solution

Let's 'spell out' the sum:

[Math Processing Error]

The sum within the brackets is exactly *[Math Processing Error]*. This is exact, and not an approximation, because we have all infinite terms.

Therefore,

[Math Processing Error]

This would require that you recognize the term within brackets as the Maclaurin series of the exponential function. One simpler version of the problem would be to ask you to prove that the sum equals 1.

There are more ways we can use Taylor series in the physical sciences. We will see another type of application when we study differential equations. In fact, power series are extremely important in finding the solutions of a large number of equations that arise in quantum mechanics. The description of atomic orbitals, for example, require that we solve differential equations that involve expressing functions as power series.

3.5: Problems

Problem 3.5.1

Expand the following functions around the value of x indicated in each case.

In each case, write down at least four terms of the series, and write down the result as an infinite sum.

- $\sin(ax)$, $x = 0$, a is a constant
- $\cos(ax)$, $x = 0$, a is a constant
- e^{ax}, $x = 0$, a is a real constant
- e^{-ax}, $x = 0$, a is a real constant
- $\ln(ax)$, $x = 1$, a is a real constant

Problem 3.5.2

Use the results of the previous problem to prove Euler's relationship:

$$e^{ix} = \cos x + i \sin x$$

Problem 3.5.3

The osmotic pressure (π) of a solution is given by

$$-RT \ln x_A = \pi V_m$$

where V_m is the molar volume of the pure solvent, and x_a is the mole fraction of the solvent.

Show that in the case of a dilute solution

$$RT x_B \approx \pi V_m$$

where x_B is the mole fraction of the solute. Remember that the mole fractions of the solute and the solvent need to add up to 1.

Note: you may use any of the results you obtained in Problem $3.5.1$.

Problem 3.5.4

The following expression is known as the Butler-Volmer equation, and it is used in electrochemistry to describe the kinetics of an electrochemical reaction controlled solely by the rate of the electrochemical charge transfer process.

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}),\ 0 < \alpha < 1 \text{ and } f > 0, \eta > 0$$

Show that $j \approx j_0 f\eta$ when $f\eta << 1$.

Note: you may use any of the results you obtained in Problem $3.5.1$.

Problem 3.5.5

The energy density of black-body radiation (ρ) at temperature T is given by Plank's formula:

$$\rho(\lambda) = \frac{8\pi hc}{\lambda^5}[e^{hc/\lambda kT} - 1]^{-1}$$

where λ is the wavelength, h is Plank's constant, and c is the speed of light. Show that the formula reduces to the classical Rayleigh-Jeans law $\rho = 8\pi kT/\lambda^4$ for long wavelengths ($\lambda \to \infty$).

Hint: Define a variable $\nu = \lambda^{-1}$ and solve the problem for $\nu \to 0$.

Note: you may use any of the results you obtained in Problem $3.5.1$.

Problem 3.5.6

Use series to prove that $\sum_{k=0}^{\infty} \frac{\lambda^k e^{-\lambda}}{k!} = 1$, λ is a positive real constant.

Problem 3.5.7

Write down the equation of a straight line that provides a good approximation of the function e^x at values close to $x = 2$.

Problem 3.5.8

Use a Taylor expansion around a to prove that $\ln x = \ln a + \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{na^n}(x-a)^n$

CHAPTER OVERVIEW

4: First Order Ordinary Differential Equations

Objectives

- Be able to identify the dependent and independent variables in a differential equation.
- Be able to identify whether an ordinary differential equation (ODE) is linear or nonlinear.
- Be able to identify the order of an ODE
- Be able to identify whether a first order ODE is separable or not.
- Be able to find the general and particular solutions of linear first order ODEs.
- Be able to find the general and particular solutions of separable first order ODEs.
- Understand how to verify that the solution you got in a problem satisfies the differential equation and initial conditions.
- Understand how to solve differential equations in the context of chemical kinetics. Understand the concept of mass balance, and half-life.

4.1: Definitions and General Concepts

A differential equation is an equation that defines a relationship between a function and one or more derivatives of that function.

For example, this is a differential equation that relates the function *[Math Processing Error]* with its first and second derivatives:

[Math Processing Error]

The above example is an **ordinary differential equation** (ODE) because the unknown function, *[Math Processing Error]*, is a function of a single variable (in this case *[Math Processing Error]*). Because we are dealing with a function of a single variable, only ordinary derivatives appear in the equation. If we were dealing with a function of two or more variables, the partial derivatives of the function would appear in the equation, and we would call this differential equation a **partial differential equation** (PDE). An example of a PDE is shown below. We will discuss PDEs towards the end of the semester.

[Math Processing Error]

Note that in the example above we got 'lazy' and used *[Math Processing Error]* instead of *[Math Processing Error]*. The fact that *[Math Processing Error]* is a function of *[Math Processing Error]*, and *[Math Processing Error]* is obvious from the derivatives, so you will see that often we will relax and not write the variables explicitly with the function.

Why do we need to study differential equations? The answer is simple: **Differential equations arise in the mathematical models that describe most physical processes**. Figure *[Math Processing Error]* illustrates three examples.

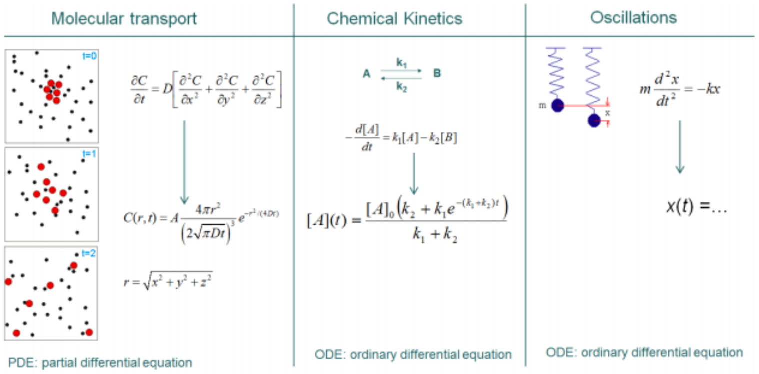


Figure *[Math Processing Error]*: Examples of physical process that are described mathematically through differential equations (CC BY-NC-SA; Marcia Levitus)

The first column illustrates the problem of molecular transport (diffusion). Suppose the red circles represent molecules of sucrose (sugar) and the black circles molecules of water, and assume you are interested in modeling the concentration of sucrose as a function of position and time after you dissolve some sucrose right in the middle of the container. The differential equation describing the process is a partial differential equation because the concentration will be a function of two variables: *[Math Processing Error]*, the distance from the origin, and *[Math Processing Error]*, the time elapsed from the moment you started the experiment. The solution shown in the figure was obtained by assuming that all the molecules of sucrose are concentrated at the center at time zero. You could solve the differential equation with other initial conditions.

The second column illustrates a chemical system where a compound A reacts to give B. The reaction is reversible, and it could, for example, represent two different isomers of the same molecule. The differential equation models how the concentration of A, [A], changes with time. We will in fact analyze this problem in detail and find the solution shown in the figure. As we will see, in this case we are also assuming certain initial conditions.

Finally, the third column illustrates a mass attached to a spring. We will also analyze this equation, and the solution is not shown because it will be your job to get it in your homework. You may think this is a physics problem, but because molecules have chemical bonds, and atoms vibrate around their equilibrium positions, systems like these are of interest to chemists as well.

To solve the differential equation means to find the function (or family of functions) that satisfies the equation. In our first example in Figure *[Math Processing Error]*, we would need to find the function C*[Math Processing Error]* that satisfies the equation. In the second example we would need to find all the functions A*[Math Processing Error]* that satisfy the equation. As we will see shortly, whether the solution is one function or a family of functions depends on whether we are restricted by initial conditions (e.g. at time zero [B] = 0) or not.

The order of a differential equation (partial or ordinary) is the highest derivative that appears in the equation. Below is an example of a first order ordinary differential equation:

[Math Processing Error]

In this example, we are looking for all the functions *[Math Processing Error]* that satisfy Equation *[Math Processing Error]*. As usual, we will call *[Math Processing Error]* the independent variable, and *[Math Processing Error]* the dependent variable. Again, *[Math Processing Error]* is of course *[Math Processing Error]*, but often we do not write this explicitly to save space and time. This is an ordinary differential equation because *[Math Processing Error]* is a function of a single variable. It is a first order differential equation because the highest derivative is of first order. It is also **a linear differential equation** because the dependent variable and all of its derivatives appear in a linear fashion. The distinction between linear and non-linear ODEs is very important because there are different methods to solve different types of differential equations. Mathematically, a first order linear ODE will have this general form:

[Math Processing Error]

It is crucial to understand that the linearity refers to the terms that include the dependent variable (in this case *[Math Processing Error]*). The terms involving *[Math Processing Error]* (*[Math Processing Error]* and *[Math Processing Error]*) can be non-linear, as in Equation *[Math Processing Error]*. An example of a non-linear differential equation is shown below. Note that the dependent variable appears in a transcendental function (in this case an exponential), and that makes this equation non-linear:

[Math Processing Error]

Analogously, a linear second order ODE will have the general form:

[Math Processing Error]

Again, we don't care whether the functions *[Math Processing Error]* and *[Math Processing Error]* are linear in *[Math Processing Error]* or not. The only thing that matters is that the terms involving the dependent variable are.

> Identifying the dependent and the independent variables: Test yourself with this short quiz. http://tinyurl.com/ll22wnv
>
> Linear or non-linear? See if you can identify the linear ODEs in this short quiz. http://tinyurl.com/msldkp3

We are still defining concepts, but we haven't said anything so far regarding how to solve differential equations! We still need to go over a few more things, so be patient.

An *[Math Processing Error]*-order differential equation together with *[Math Processing Error]* auxiliary conditions imposed at the same value of the independent variable is called an **initial value problem**. For example, we may be interested in finding the function *[Math Processing Error]* that satisfies the following conditions:

[Math Processing Error]

Notice that we are introducing different types of notations so you get used to seeing mathematical equations in different 'flavors'. Here, *[Math Processing Error]* of course means *[Math Processing Error]*. This is an initial value problem because we have a second-order differential equation with two auxiliary conditions imposed at the same value of *[Math Processing Error]* (in this case *[Math Processing Error]*). There are infinite functions *[Math Processing Error]* that satisfy *[Math Processing Error]*, but only one will also satisfy the two initial conditions we imposed. If we were dealing with a first order differential equation we would need only one initial condition. We would need three for a third-order differential equation.

How do we use initial conditions to find a solution? In general, the solution of a second order ODE will contain two arbitrary constants (in the example below *[Math Processing Error]* and *[Math Processing Error]*). This is what we will call the **general solution** of the differential equation. For example,

[Math Processing Error] is the general solution of *[Math Processing Error]*. We can verify this is true by taking the second derivative of this function. Again, we do not know yet how to get these solutions, but if we are given this solution, we know how to check if it is correct. It is clear that *[Math Processing Error]* and *[Math Processing Error]* can be in principle anything, so the solution of the ODE is a whole family of functions. However, if we are given initial conditions we are looking for a **particular solution**, one that not only satisfies the ODE, but also the initial conditions. Which function is that?

The first initial condition states that *[Math Processing Error]*. Therefore,

[Math Processing Error]

[Math Processing Error]

So far, we demonstrated that the functions *[Math Processing Error]* satisfy not only the ODE, but also the initial condition *[Math Processing Error]*. We still have another initial condition, which will allow us to determine the value of *[Math Processing Error]*.

[Math Processing Error]

[Math Processing Error]

Therefore, the function *[Math Processing Error]* is the **particular solution** of the initial value problem described in Equation *[Math Processing Error]*. We can check our answer by verifying that this solution satisfies the three equations of the initial value problem:

1. *[Math Processing Error]* *[Math Processing Error]*, so we know that the solution we found satisfies the differential equation.
2. *[Math Processing Error]*e*[Math Processing Error]*, so we know that the solution we found satisfies one of the initial conditions.
3. *[Math Processing Error][Math Processing Error]*, so we know that the solution we found satisfies the other initial condition as well.

Therefore, we demonstrated that *[Math Processing Error]* is indeed the solution of the problem.

An *[Math Processing Error]*-order differential equation together with *[Math Processing Error]* auxiliary conditions imposed at more than one value of the independent variable is called a **boundary value problem**. What is the difference between a boundary value problem and an initial value problem? In the first case, the conditions are imposed at different values of the independent variable, while in the second case, as we just saw, the conditions are imposed at the same value of the independent variable. For example, this would be a boundary value problem:

[Math Processing Error]

Notice that we still have two conditions because we are dealing with a second order differential equation. However, one condition deals with *[Math Processing Error]* and the other with *[Math Processing Error]*. The conditions can refer to values of the first derivative, as in the previous example, or to values of the function itself, as in the example of Equation *[Math Processing Error]*.

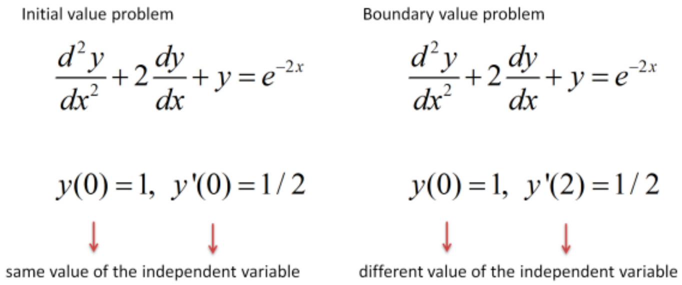


Figure *[Math Processing Error]*: Initial vs boundary value problems (CC BY-NC-SA; Marcia Levitus)

Why do we need to distinguish between initial value and boundary value problems? The reason lies in a theorem that states that, for linear ODEs, the solution of a initial value problem exists and is unique, but a boundary value problem does not have the existence and uniqueness guarantee. The theorem is not that simple (for example it requires that the functions in *[Math Processing Error]* (*[Math Processing Error]* in Equation *[Math Processing Error]*) are continuous), but the bottom line is that we may find a solution whenever the conditions are imposed at the same value of *[Math Processing Error]*, but we may not find a solution whenever the conditions are imposed at different values. We will see examples when we discuss second order ODEs, and in particular we will discuss how boundary conditions give rise to interesting physical phenomena. For example, we will see that boundary conditions are responsible for the fact that energies in atoms and molecules are quantized.

Coming back to the boundary value problem of Equation *[Math Processing Error]*, it is important to recognize that because the actual differential equation is the same as in the example of Equation *[Math Processing Error]*, the **general solution** is still the same: *[Math Processing Error]*. However, the **particular solution** will be different (different values of *[Math Processing Error]* and *[Math Processing Error]*), because we need to satisfy different conditions.

As in the first example, the first boundary condition states that *[Math Processing Error]* so:

[Math Processing Error]

[Math Processing Error]

as before. However, now

[Math Processing Error]

where we have used the result *[Math Processing Error]* so

[Math Processing Error]

and the **particular solution** is therefore *[Math Processing Error]*. As we did before, it is important that we check our solution. If we are right, this solution needs to satisfy all the relationships stated in Equation *[Math Processing Error]*.

1. *[Math Processing Error] [Math Processing Error]*, so the solution satisfies the differential equation.
2. *[Math Processing Error]*e*[Math Processing Error]*, so our solution satisfies one of the boundary conditions.
3. *[Math Processing Error][Math Processing Error]*, so our solution satisfies the other boundary condition as well.

Figure *[Math Processing Error]* illustrates the difference between the general solution and the particular solution. The general solution has two arbitrary constants, so there are an infinite number of functions that satisfy the differential equation. Three examples are shown in different colors. However, only one of these satisfies both boundary conditions (shown with the arrows).

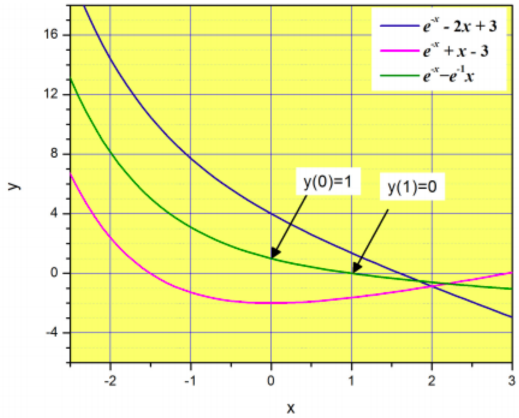


Figure *[Math Processing Error]*: General and particular solutions of boundary value problem [eq3] (CC BY-NC-SA; Marcia Levitus)

> Using boundary conditions: see if you can obtain the particular solution of a second order ODE in this short quiz. http://tinyurl.com/lovh4x3

So far we have discussed how to:

- Identify the dependent and independent variables
- Identify the order of the differential equation.
- Identify whether the equation is linear or not
- Use initial or boundary conditions to obtain particular solutions from general solutions
- Check your results to be sure you satisfy the differential equation and all the initial or boundary conditions

We are obviously missing the most important question: How do we solve the differential equation? Unfortunately, there is no universal method, and in fact some differential equations cannot be solved analytically. We will see some examples of equations that cannot be solved analytically and we will discuss what can be done in those cases. In this class we will only discuss some differential equations of interest in physical chemistry. It is not our intention to cover the topic in a comprehensive manner, and we will not touch on other differential equations that might be of interest in other disciplines. Yet, the background you will get in this class will allow you to teach yourself more advanced topics in differential equations if your future career demands that you have a deeper knowledge of the subject.

4.2: 1st Order Ordinary Differential Equations

We will discuss only two types of 1st order ODEs, which are the most common in the chemical sciences: **linear** 1st order ODEs, and **separable** 1st order ODEs. These two categories are not mutually exclusive, meaning that some equations can be both linear and separable, or neither linear nor separable.

Separable 1st order ODEs

An ODE is called separable if it can be written as

$$\frac{dy}{dx}=\frac{g(x)}{h(y)} \tag{4.2.1}$$

A separable differential equation is the easiest to solve because it readily reduces to a problem of integration:

$$\int h(y)dy=\int g(x)dx \tag{4.2.2}$$

For example: $\frac{dy}{dx}=4y^2x$ can be written as $y^{-2}dy=4xdx$ or $\frac{1}{4}y^{-2}dy=xdx$. This equation is separable becuase the terms multiplying dy do not contain any terms involving x, and the terms multiplying dx do not contain any terms involving y. This allows you to integrate and solve for $y(x)$:

$$\begin{aligned}\int y^{-2}dy&=\int 4xdx\\ -\frac{1}{y}+c_1&=2x^2+c_2\\ y&=-\frac{1}{2x^2+c_3}\end{aligned}$$

where $c_3=c_2-c_1$.

Let’s see how to separate other equations. If you wanted to finish these problems you would integrate both sides and solve for the dependent variable, as shown in the solved examples below. For now, let’s concentrate on how to separate the terms involving the independent variable from the terms involving the dependent variable:

Example 1:

$$\begin{gathered}y'=e^{-y}(3-x)\\ \frac{dy}{dx}=e^{-y}(3-x)\end{gathered}$$

Separated ODE:

$$e^y dy=(3-x)dx$$

Example 2:

$$\begin{gathered}\theta'=\frac{t^2}{\theta}\\ \frac{d\theta}{dt}=\frac{t^2}{\theta}\end{gathered}$$

Separated ODE:

$$\theta d\theta=t^2dt$$

Example 3:

$$\frac{dA(t)}{dt}=\frac{2-t}{1-A(t)}$$

Separated ODE:

$$(1-A(t))dA=(2-t)dt$$

✓ Example $4.2.1$

Solve the following differential equation: $\frac{dy}{dx}=yx^2$

Solution

We first ‘separate’ the terms involving y from the terms involving x:

$$\frac{1}{y}dy=x^2dx$$

and then integrate both sides (it is crucial not to forget the integration constants):

$$\int\frac{1}{y}dy=\int x^2dx\to\ln y+c_1=\frac{1}{3}x^3+c_2$$

Remember that our goal is to find $y(x)$, so our job now is to solve for y:

$$\begin{aligned}\ln y+c_1&=\frac{1}{3}x^3+c_2\\ \ln y&=\frac{1}{3}x^3+c_2-c_1\\ &=\frac{1}{3}x^3+c_3\end{aligned}$$

$$y=\exp\left(\frac{1}{3}x^3+c_3\right)=\exp\left(\frac{1}{3}x^3\right)\exp(c_3)=Ke^{x^3/3}$$

Notice that c_2-c_1 is a constant, so we re-named it c_3. In addition, $exp(c_3)$ is also a constant, so we re-named it K. The names of the constants are not important.

Just to be on the safe side, let’s verify that $Ke^{x^3/3}$ is indeed the solution of this differential equation. We’ll do it by substitution. On the left-hand side of the equation we have $\frac{dy}{dx}$, and on the right-hand side we have yx^2. We’ll replace y by $Ke^{x^3/3}$ on both sides, and verify that the two sides are identical (the equality holds).

$$\frac{dy}{dx}=Ke^{x^3/3}x^2$$

$$yx^2=Ke^{x^3/3}x^2$$

We just verified that the function $Ke^{x^3/3}$ satisfies $\frac{dy}{dx}=yx^2$, so we know our solution is correct!

Example $4.2.1$ illustrates why you need to be very comfortable with the properties of the logarithmic and exponential functions. These functions appear everywhere in the physical sciences, so if you found this challenging you need to review your algebra!

✓ Example $4.2.2$

Solve the following differential equation: $\frac{dx}{dt}=x^2t$

This might look similar to example $4.2.1$, but notice that in this case, x is the dependent variable.

Solution

We first ‘separate’ the terms involving x from the terms involving t:

$$\frac{1}{x^2}dx=tdt$$

and then integrate both sides (it is crucial not to forget the integration constants):

$$\int \frac{1}{x^2}dx = \int tdt \rightarrow -x^{-1} + c_1 = t^2/2 + c_2$$

Remember that our goal is to find $x(t)$, so our job now is to solve for x:

$$-x^{-1} + c_1 = t^2/2 + c_2$$

$$x^{-1} = -t^2/2 + (c_1 - c_2)$$

$$x(t) = -\frac{1}{\frac{t^2}{2} + (c_2 - c_1)} = -\frac{1}{t^2/2 + c}.$$

where $c = (c_2 - c_1)$.

Just to be on the safe side, let's verify that our solution satisfies the differential equation. We'll do it by substitution. On the left-hand side of the equation we have $\frac{dx}{dt}$, and on the right-hand side we have tx^2. We'll replace x by $-\frac{1}{t^2/2+c}$ on both sides, and verify that the two sides are identical (the equality holds).

$$\frac{dx}{dt} = \frac{t}{(t^2/2 + c)^2}$$

$$x^2 t = \frac{t}{(t^2/2 + c)^2}$$

We just verified that the function $-\frac{1}{t^2/2+c}$ satisfies $\frac{dx}{dt} = tx^2$, so we know our solution is correct!

This example is also available as a video: http://tinyurl.com/kxdfqxq

Watch an additional solved example. http://tinyurl.com/kem7e6h

External Links:

- Example 1: http://patrickjmt.com/separable-differential-equation-example-2
- Example 2: http://www.youtube.com/watch?v=76WdBlGpxVw
- Example 3: http://www.youtube.com/watch?v=3jpiW_oueaA

Linear 1st order ODEs

A general first-order linear ODE can be written

$$\frac{dy}{dx} + p(x)y = q(x) \tag{4.2.3}$$

Note that the linearity refers to the y and dy/dx terms, $p(x)$ and $q(x)$ do not need to be linear in x. You may need to reorganize terms around to write your equation in the form shown in Equation 4.2.3. For example, $dy = (8e^x - 3y)dx$ is linear, because it can be re-organized as

$$\frac{dy}{dx} + 3y = 8e^x \tag{4.2.4}$$

Comparing Equations 4.2.3 and 4.2.4, we see that in this case, $p(x) = 3$ and $q(x) = 8e^x$. In this example $p(x)$ is a constant, but this need not to be the case. The term $p(x)$ can be any function of x.

First order linear ODEs can be solved by multiplying by the integrating factor $e^{\int p(x)dx}$. This sounds very strange at first sight, but we will see how it works with the example of Equation 4.2.4.

Our very first step is to write the equation so it looks like Equation 4.2.3. We then calculate the integrating factor, in this case $e^{\int 3dx} = e^{3x}$. We next multiply both sides of the equation by the integrating factor:

$$\frac{dy}{dx}e^{3x}+3ye^{3x}=8e^{x}e^{3x}=8e^{4x}$$

In the next step, we recognize that the left-hand side is the derivative of the dependent variable multiplied by the integrating factor:

$$\frac{dy}{dx}e^{3x}+3ye^{3x}=\frac{d}{dx}(ye^{3x})$$

This last step is the multiplication rule in reverse. If you start with $\frac{d}{dx}(ye^{3x})$, you can apply the multiplication rule to obtain $\frac{dy}{dx}e^{3x}+3ye^{3x}$. The whole point of calculating the integrating factor is that it guarantees that the left-hand side of the equation will always be the derivative of the dependent variable multiplied by the integrating factor. This will allow us to move dx to the right side, and integrate:

$$\frac{d}{dx}(ye^{3x})=8e^{4x}$$

$$d(ye^{3x})=8e^{4x}dx$$

$$\int d(ye^{3x})=\int 8e^{4x}dx$$

The left-side of the above equation is $\int d(ye^{3x})=ye^{3x}$, in the same way that $\int dy=y$. The right side is $\int 8e^{4x}dx=2e^{4x}+c$. Note that we included the integration constant only on one side. This is because we already saw that if we included integration constants in both sides we could group them into a single constant.

So far we have

$$ye^{3x}=2e^{4x}+c$$

Now we need to solve for the dependent variable, in this case $y(x)$. Dividing both terms by e^{3x}:

$$y=2e^{x}+ce^{-3x}$$

which is the general solution of Equation 4.2.4. Before moving on let's verify that this function satisfies Equation 4.2.4 by substituting y by $y=2e^{x}+ce^{-3x}$:

$$\frac{dy}{dx}=2e^{x}-3ce^{-3x}$$

$$3y=6e^{x}+3ce^{-3x}$$

$$\frac{dy}{dx}+3y=2e^{x}-3ce^{-3x}+6e^{x}+3ce^{-3x}=8e^{x}$$

which equals the right-hand side of Equation 4.2.4. This verifies that $y=2e^{x}+ce^{-3x}$ is indeed the general solution of Equation 4.2.4. If we were given an initial condition we could calculate the value of c and obtain the particular solution.
Let's review and list the steps we used to find the solution of a linear 1st order ODE:

1. Re-arrange the terms so the equation has the form $\frac{dy}{dx}+p(x)y=q(x)$
2. Multiply both sides of the equation by the integrating factor $e^{\int p(x)dx}$
3. Recognize that the left-hand side can be written as $\frac{d}{dx}\left(ye^{\int p(x)dx}\right)$
4. Move dx to the right-hand side and integrate. Remember the integration constants!
5. Solve for the dependent variable
6. If given, use the initial condition to calculate the value of the arbitrary constant.
7. Verify your solution is correct by substitution into the differential equation.

> See another solved example to see this method in action: http://tinyurl.com/lzluktp
>
> External Links: http://www.youtube.com/watch?v=HAb9JbBD2ig

4.3: Chemical Kinetics

The term chemical kinetics refers to the study of the rates of chemical reactions. As we will see, differential equations play a central role in the mathematical treatment of chemical kinetics. We will start with the simplest examples, and then we will move to more complex cases. As you will see, in this section we will focus on a couple of reaction mechanisms. The common theme will be to find expressions that will allow us to calculate the concentration of the different species that take part of the reaction at different reaction times.

Let's start with the simplest case, in which a reactant A reacts to give the product B. We'll assume the reaction proceeds in one step, meaning there are no intermediates that can be detected.

[Math Processing Error]

We'll use the following notation for the time-dependent concentrations of A and B: [A]*[Math Processing Error]*, [B]*[Math Processing Error]*, or simply [A] and [B]. We'll use [A]*[Math Processing Error]* and [B]*[Math Processing Error]* to denote the concentrations of A and B at time *[Math Processing Error]*. The constant *[Math Processing Error]* is the rate constant of the reaction, and is a measure of how fast or slow the reaction is. It depends on the reaction itself (the chemical compounds A and B) and environmental factors such as temperature. The rate constant does not depend on the concentrations of the species involved in the reaction. The units of *[Math Processing Error]* depend on the particular mechanism of the reaction, as we will see through the examples. For the case described above, the units will be 1/time (e.g. *[Math Processing Error]*)

The rate of the reaction (*[Math Processing Error]*) will be defined as the number of moles of A that disappear or the number of moles of B that appear per unit of time (e.g. per second) and volume (e.g. liter). This is true because of the stoichiometry of the reaction, as we will discuss in a moment. However, because the rate is a positive quantity, we will use a negative sign if we look at the disappearance of A:

[Math Processing Error]

The rate of the reaction, therefore, is a positive quantity with units of M.s*[Math Processing Error]*, or in general, concentration per unit of time. As we will see, the rate of the reaction depends on the actual concentration of reactant, and therefore will in general decrease as the reaction progresses and the reactant is converted into product. Although all the molecules of A are identical, they do not need to react at the same instant. Consider the simple mechanism of Equation *[Math Processing Error]*, and imagine that every molecule of A has a probability *[Math Processing Error]* of reacting in every one-second interval. Suppose you start with 1 mole of A in a 1 L flask (*[Math Processing Error]*), and you measure the concentration of A one second later. How many moles of A do you expect to see? To answer this question, you can imagine that you get everybody in China (about one billion people) to throw a die at the same time, and that everybody who gets a six wins the game. How many winners do you expect to see? You know that the probability that each individual gets a six is *[Math Processing Error]*, and therefore one-sixth of the players will win in one round of the game. Therefore, you can predict that the number of winers will be *[Math Processing Error]*, and the number of losers will be *[Math Processing Error]*. If we get the losers to play a second round, we expect that one-sixth of them will get a six, which accounts for *[Math Processing Error]* people. After the second run, therefore, we'll still have *[Math Processing Error]* losers.

Following the same logic, the probability that a molecule of A reacts to give B in each one-second interval is *[Math Processing Error]*, and therefore in the first second you expect that *[Math Processing Error]* molecules react and *[Math Processing Error]* remain unreacted. In other words, during the first second of your reaction 0.001 moles of A were converted into B, and therefore the rate of the reaction was *[Math Processing Error]*. During the second one-second interval of the reaction you expect that one-thousand of the remaining molecules will react, and so on. Imagine that you come back one hour later (3,600 s). We expect that *[Math Processing Error]* molecules will remain unreacted, which is about *[Math Processing Error]* molecules. If you measure the reaction rate in the next second, you expect that one-thousand of them (*[Math Processing Error]* molecules, or *[Math Processing Error]* moles) will react to give B. The rate of the reaction, therefore, decreased from *[Math Processing Error]* at *[Math Processing Error]* to *[Math Processing Error]* at *[Math Processing Error]*. You should notice that the fraction of molecules of A that react in each one-second is always the same (in this case one-thousand). Therefore, the number of molecules that react per time interval is proportional to the number of molecules of A that remain unreacted at any given time. We just concluded that the rate of the reaction is proportional to the concentration of A:

[Math Processing Error]

The proportionality constant, *[Math Processing Error]*, is related to the probability that a molecule will react in a small time interval, as we discussed above. In this class, we will concentrate on solving differential equations such as the one above. This is a very simple differential equation that can be solved using different initial conditions. Let's say that our goal is to find both [A] *[Math Processing Error]* and [B]*[Math Processing Error]*. As chemists, we need to keep in mind that the law of mass conservation requires that

[Math Processing Error]

In plain English, the concentrations of A and B at any time need to add up to the sum of the initial concentrations, as one molecule of A converts into B, and we cannot create or destroy matter. Again, keep in mind that this equation will need to be modified according to the stoichiometry of the reaction. We will call an equation of this type a 'mass balance'.

Before solving this equation, let's look at other examples. What are the differential equations that describe this sequential mechanism?

[Math Processing Error]

In this mechanism, A is converted into C through an intermediate, B. Everything we discussed so far will apply to each of these two elementary reactions (the two that make up the overall mechanism). From the point of view of A nothing changes. Because the rate of the first reaction does not depend on B, it is irrelevant that B is converted into C (imagine you give 1 dollar per day to a friend. It does not matter whether you friend saves the money or gives it to someone else, you still lose 1 dollar per day).

[Math Processing Error]

On the other hand, the rate of change of [B], *[Math Processing Error]* is the sum of the rate at which B is created (*[Math Processing Error]*), minus the rate at which it disappears by reacting into C (*[Math Processing Error]*):

[Math Processing Error]

This can be read: The rate of change of [B] equals the rate at which [B] appears from A into B, minus the rate at which [B] disappears from B into C. In each term, the rate is proportional to the reactant of the corresponding step: A for the first reaction, and B for the second step.

What about C? Again, it is irrelevant that B was created from A (if you get 1 dollar a day from your friend, you don't care if she got it from her parents, you still get 1 dollar per day). The rate at which C appears is proportional to the reactant in the second step: B. Therefore:

[Math Processing Error]

The last three equations form a system of differential equations that need to be solved considering the initial conditions of the problem (e.g. initially we have A but not B or C). We'll solve this problem in a moment, but we still need to discuss a few issues related to how we write the differential equations that describe a particular mechanism. Imagine that we are interested in

[Math Processing Error]

We know that the rate of a reaction is defined as the change in concentration with time...but which concentration? is it *[Math Processing Error]*? or *[Math Processing Error]*? or *[Math Processing Error]*? These are all different because 3 molecules of C are created each time 1 of B and 2 of A disappear. Which one should we use? Because 2 of A disappear every time 1 of B disappears: *[Math Processing Error]*. Now, considering that rates are positive quantities, and that the derivatives for the reactants, *[Math Processing Error]* and *[Math Processing Error]*, are negative:

[Math Processing Error]

This example shows how to deal with the stoichiometric coefficients of the reaction. Note that in all our examples we assume that the reactions proceed as written, without any 'hidden' intermediate steps.

First order reactions

We have covered enough background, so we can start solving the mechanisms we introduced. Let's start with the easiest one (Equations *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*):

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

This mechanism is called a first order reaction because the rate is proportional to the first power of the concentration of reactant. For a second-order reaction, the rate is proportional to the square of the concentration of reactant (see Problem *[Math Processing Error]*). Let's start by finding *[Math Processing Error]* from *[Math Processing Error]*. We'll then obtain*[Math Processing Error]* from the mass balance. This is a very simple differential equation because it is separable:

[Math Processing Error]

[Math Processing Error]

We integrate both sides of the equation, and combine the two integration constants in one:

[Math Processing Error]

We need to solve for [A]:

[Math Processing Error]

This is the general solution of the problem. Let's assume we are giving the following initial conditions: [A]*[Math Processing Error]*, [B]*[Math Processing Error]* We'll use this information to find the arbitrary constant *[Math Processing Error]*:

[Math Processing Error]

Therefore, the particular solution is:

[Math Processing Error]

What about [B]? From the mass balance, [B] = [A]*[Math Processing Error]* + [B]*[Math Processing Error]* - [A] = [A]*[Math Processing Error]* - [A]*[Math Processing Error]*.

Figure *[Math Processing Error]* shows three examples of decays with different rate constants.

We can calculate the half-life of the reaction (*[Math Processing Error]*), defined as the time required for half the initial concentration of A to react. From Equation *[Math Processing Error]*:

[Math Processing Error]

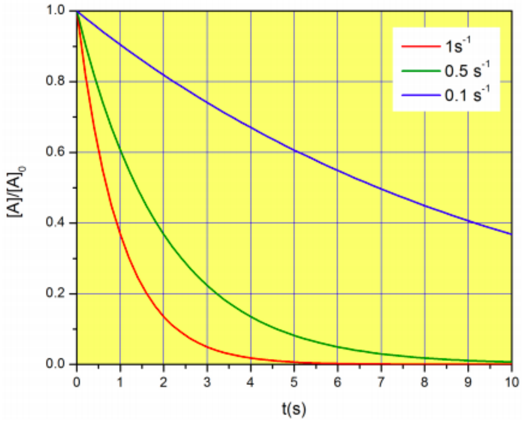


Figure *[Math Processing Error]*: Time-dependent concentration of the reactant in the reaction *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

When *[Math Processing Error]*,

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

Note that in this case, the half-life does not depend on the initial concentration of A. This will not be the case for other types of mechanisms. Also, notice that we have already covered the concept of half-life in Chapter 1 (see Figure *[Math Processing Error]*), so this might be a good time to read that section again and refresh what we have already learned about sketching exponential decays.

In physical chemistry, scientists often talk about the 'relaxation time' instead of the half-life. The relaxation time *[Math Processing Error]* for a decay of the shape *[Math Processing Error]* is *[Math Processing Error]*, so in this case, the relaxation time is simply *[Math Processing Error]*. Notice that the relaxation time has units of time, and it represents the time at which the concentration has decayed to *[Math Processing Error]* of its original value:

[Math Processing Error]

The half-life and relaxation time are compared in Figure *[Math Processing Error]* for a reaction with *[Math Processing Error]*.

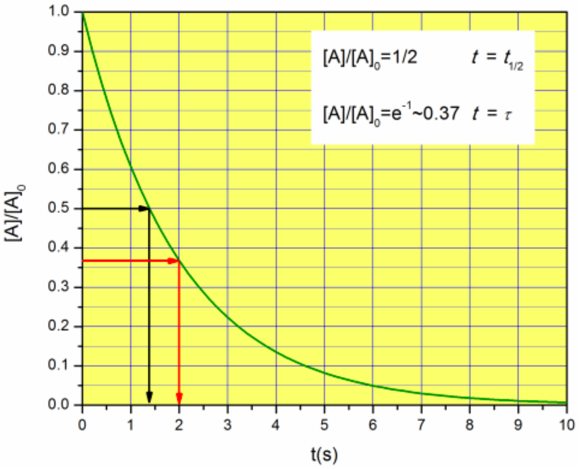


Figure *[Math Processing Error]*: Half-life (black) and relaxation time (red) for the reaction *[Math Processing Error]* with *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

Consecutive First Order Processes

We will now analyze a more complex mechanism, which involves the formation of an intermediate species (B):

[Math Processing Error]

which is mathematically described by Equations *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*. Let's assume that initially the concentration of A is [A]*[Math Processing Error]*, and the concentrations of B and C are zero. In addition, we can write a mass balance, which for these initial conditions is expressed as:

[Math Processing Error]

Let's summarize the equations we have:

[Math Processing Error] [Math Processing Error] [Math Processing Error] [Math Processing Error] [Math Processing Error] [Math Processing Error]

Note that Equation *[Math Processing Error]* is not independent from Equations *[Math Processing Error]*-*[Math Processing Error]*. If you take the derivative of *[Math Processing Error]* you get *[Math Processing Error]*, which is the same you get if you add Equations *[Math Processing Error]*-*[Math Processing Error]*. This means that Equations *[Math Processing Error]*-*[Math Processing Error]* are not all independent, and three of them are enough for us to solve the problem. As you will see, the mass balance (*[Math Processing Error]*) will give us a very easy way of solving for [C] once we have [A] and [B], so we will use it instead of Equation *[Math Processing Error]*.

We need to solve the system of Equations *[Math Processing Error]*-*[Math Processing Error]*, and although there are methods to solve systems of differential equations (e.g. using linear algebra), this one is easy enough that can be solved with what we learned so far. This is because not all equations contain all variables. In particular, Equation *[Math Processing Error]* is a simple separable equation with dependent variable [A], which can be solved independently of [B] and [C]. We in fact just solved this equation in the First Order Reactions section, so let's write down the result:

[Math Processing Error]

Equation *[Math Processing Error]* contains two dependent variables, but luckily we just obtained an expression for one of them. We can now re-write *[Math Processing Error]* as:

[Math Processing Error]

Equation [Math Processing Error] contains only one dependent variable, [B], one independent variable, [Math Processing Error], and three constants: [Math Processing Error], [Math Processing Error] and [Math Processing Error]. This is therefore an ordinary differential equation, and if it is either separable or linear, we will be able to solve it with the techniques we learned in this chapter. Recall eq. [sep], and verify that Equation [Math Processing Error] cannot be separated as

[Math Processing Error]

Equation [Math Processing Error] is not separable. Is it linear? Recall Equation [Math Processing Error] and check if you can write this equation as [Math Processing Error]. We in fact can:

[Math Processing Error]

Let's use the list of steps delineated in Section 4.2. We need to calculate the integrating factor, [Math Processing Error], which in this case is [Math Processing Error]. We then multiply Equation [Math Processing Error] by the integrating factor:

[Math Processing Error]

In the next step, we need to recognize that the left-hand side of the equation is the derivative of the product of the dependent variable times the integrating factor:

[Math Processing Error]

We then take '[Math Processing Error]' to the right side of the equation and integrate both sides:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

We have an arbitrary constant because this is a first order differential equation. Let's calculate [Math Processing Error] using the initial condition [Math Processing Error]:

[Math Processing Error]

[Math Processing Error]

And therefore,

[Math Processing Error]

[Math Processing Error]

Before moving on, notice that we have assumed that [Math Processing Error]. We were not explicit, but we performed the integration with this assumption. If [Math Processing Error] the exponential term becomes 1, which is not a function of [Math Processing Error]. In this case, the integral will obviously be different, so our answer assumes [Math Processing Error]. This is good news, since otherwise we would need to worry about the denominator of [eq:b(t)] being zero. You will solve the case [Math Processing Error] in Problem 4.4.

Now that we have [A] and [B], we can get the expression for [C]. We could use Equation [Math Processing Error]:

[Math Processing Error]

This is not too difficult because the equation is separable. However, it is easier to get [C] from the mass balance, Equation [Math Processing Error]:

[Math Processing Error]

Plugging the answers we got for [A] and [B]:

[Math Processing Error]

[Math Processing Error]

Equations [Math Processing Error], [Math Processing Error], [Math Processing Error] are the solutions we were looking for. If we had the values of [Math Processing Error] and [Math Processing Error] we could plot [Math Processing Error], [Math

Processing Error] and *[Math Processing Error]* and see how the three species evolve with time. If we had *[Math Processing Error]* we could plot the actual concentrations, but notice that this does not add too much, because it just re-scales the *[Math Processing Error]*axis but does not change the shape of the curves.

Figure *[Math Processing Error]* shows the concentration profiles for a reaction with *[Math Processing Error]* and *[Math Processing Error]*. Notice that because B is an intermediate, its concentration first increases, but then decreases as B is converted into C. The product C has a 'lag phase', because we need to wait until enough B is formed before we can see the concentration of C increase (first couple of seconds in this example). As you will see after solving your homework problems, the time at which the intermediate (B) achieves its maximum concentration depends on both *[Math Processing Error]* and *[Math Processing Error]*.

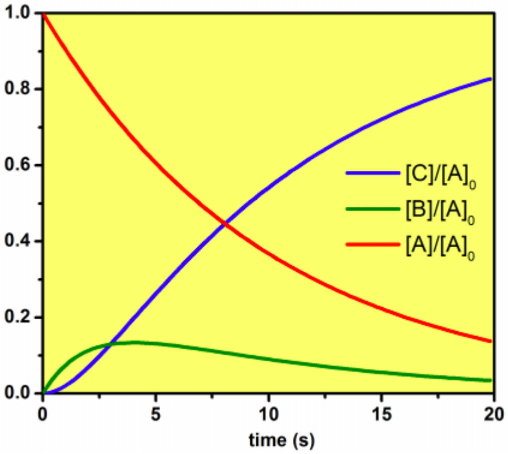


Figure *[Math Processing Error]*: Concentration profiles for the reaction *[Math Processing Error]* with *[Math Processing Error]* and *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

Reversible first order reactions

So far we have discussed irreversible reactions. Yet, we know that many reactions are reversible, meaning that the reactant and product exist in equilibrium:

[Math Processing Error]

The rate of change of [A], *[Math Processing Error]*, is the rate at which A appears (*[Math Processing Error]*) minus the rate at which A disappears (*[Math Processing Error]*):

[Math Processing Error]

We cannot solve this equation as it is, because it has two dependent variables, [A] and [B]. However, we can write [B] in terms of [A], or [A] in terms of [B], by using the mass balance:

[Math Processing Error]

[Math Processing Error]

[Math Processing Error]

This is an ordinary, separable, first order differential equation, so it can be solved by direct integration. You will solve this problem in your homework, so let's skip the steps and jump to the answer:

[Math Processing Error]

This is a reversible reaction, so if we wait long enough it will reach equilibrium The concentration of [A] in equilibrium, [A]*[Math Processing Error]*, is the limit of the previous expression when *[Math Processing Error]*. Because *[Math Processing Error]* when *[Math Processing Error]*:

[Math Processing Error]

and we can re-write Equation *[Math Processing Error]* as

[Math Processing Error]

As you will do in your homework, we can calculate *[Math Processing Error]* from the mass balance as *[Math Processing Error]*.

Equation *[Math Processing Error]* is not too different from Equation *[Math Processing Error]*. In the case of an irreversible reaction, (Equation *[Math Processing Error]*), [A] decays from an initial value [A]*[Math Processing Error]* to a final value *[Math Processing Error]* with a relaxation time *[Math Processing Error]*. For the reversible reaction, *[Math Processing Error]* decays from an initial value *[Math Processing Error]* to a final value *[Math Processing Error]* with a relaxation time *[Math Processing Error]*. This last statement is not trivial! It says that the rate at which a reaction approaches equilibrium depends on the sum of the forward and backward rate constants.

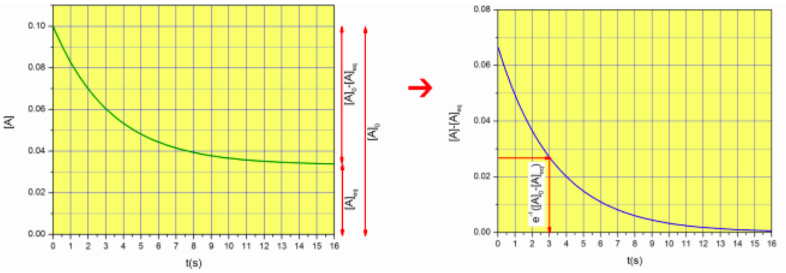


Figure *[Math Processing Error]*: The kinetics of a reaction with *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]* approaching equilibrium. Note that the relaxation time is *[Math Processing Error]* (CC BY-NC-SA; Marcia Levitus)

In your homework you will be asked to prove that the ratio of the concentrations in equilibrium, *[Math Processing Error]* is equal to the ratio of the forward and backwards rate constants. In addition, from your introductory chemistry courses you should know that the equilibrium constant of a reaction (*[Math Processing Error]*) is the ratio of the equilibrium concentrations of product of reactant. Therefore:

[Math Processing Error]

This means that we can calculate the ratio of *[Math Processing Error]* and *[Math Processing Error]* from the concentrations of A and B we observe once equilibrium has been reached (i.e. once *[Math Processing Error]*). At the same time, we can obtain the sum of *[Math Processing Error]* and *[Math Processing Error]* from the relaxation time of the process. If we have the sum and the ratio, we can calculate both *[Math Processing Error]* and *[Math Processing Error]*. This all makes sense, but it requires that we can watch the reaction from an initial state outside equilibrium. If the system is already in equilibrium, *[Math Processing Error]*, and *[Math Processing Error]* at all times. A plot of [A]*[Math Processing Error]* will look flat, and we will not be able to extract the relaxation time of the reaction. If, however, we have an experimental way of shifting the equilibrium so *[Math Processing Error]*, we can measure the relaxation time by observing how the reaction returns to its equilibrium position.

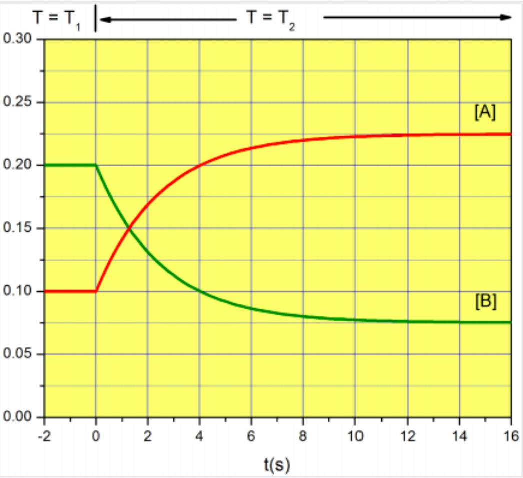
Advanced topic: How can we shift the equilibrium? One way is to produce a very quick change in the temperature of the system. The equilibrium constant of a reaction usually depends on temperature, so if a system is equilibrated at a given temperature (say *[Math Processing Error]*), and we suddenly increase the temperature (e.g. to *[Math Processing Error]*), the reaction will suddenly be away from its equilibrium condition at the new temperature. We can watch the system relax to the equilibrium concentrations at *[Math Processing Error]*, and measure the relaxation time. This will allow us to calculate the rate constants at *[Math Processing Error]*.

[Math Processing Error]

Example *[Math Processing Error]*

Advanced topic The following figure illustrates the experimental procedure known as “T-jump”, in which a sudden change in temperature is used to shift the position of a reversible reaction out of equilibrium. The experiment starts at a temperature *[Math Processing Error]*, and the temperature is increased to *[Math Processing Error]* instantaneously at time *[Math Processing Error]*. Because the equilibrium constant at *[Math Processing Error]* is different from the equilibrium constant at *[Math Processing Error]*, the system needs to relax to the new equilibrium state. From the graph below estimate to the best of your abilities *[Math Processing Error]*, *[Math Processing Error]*, and the rate constants *[Math Processing Error]*, and *[Math Processing Error]* at *[Math Processing Error]*.

[Math Processing Error]



Solution

At *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*. The equilibrium constant is *[Math Processing Error]*.

At *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*. The equilibrium constant is *[Math Processing Error]*.

Because *[Math Processing Error]*, at *[Math Processing Error]*, *[Math Processing Error]*. To calculate the relaxation time let's look at the expression for *[Math Processing Error]* (Equation *[Math Processing Error]*).

[Math Processing Error]

When the time equals the relaxation time (*[Math Processing Error]*),

[Math Processing Error]

[Math Processing Error]^1

From the graph, *[Math Processing Error]* at *[Math Processing Error]*, and therefore the relaxation time is *[Math Processing Error]*.

We have *[Math Processing Error]* and *[Math Processing Error]*:

[Math Processing Error]

4.4: Problems

Problem *[Math Processing Error]*

In each case,

- Identify the dependent and independent variables.
- Determine if the differential equation is separable.
- Determine if the differential equation is linear.
- Find the general solution.
- Find the particular solution using the given initial condition.
- Verify that your solution satisfies the differential equation by substitution.

1. *[Math Processing Error]*
2. *[Math Processing Error]*
3. *[Math Processing Error]*
4. *[Math Processing Error]*
5. *[Math Processing Error]*

Problem *[Math Processing Error]*

Consider the reaction *[Math Processing Error]*. The rate of disappearance of A is proportional to the concentration of A, so:

[Math Processing Error]

1) Obtain [A]*[Math Processing Error]* and [B]*[Math Processing Error]*.

2) Using the definition of half-life *[Math Processing Error]*, obtain an expression for *[Math Processing Error]* for this mechanism. Your result will be a function of *[Math Processing Error]*.

3) Sketch *[Math Processing Error]* and *[Math Processing Error]* for the case *[Math Processing Error]*, *[Math Processing Error]* and *[Math Processing Error]*. Remember that you are expected to do this without the help of a calculator.

Problem *[Math Processing Error]*

Consider the reaction *[Math Processing Error]*. This mechanism is called a bi-molecular reaction, because the reaction involves the collision of two molecules of reactant. In this case, the rate of disappearance of A is proportional to the square of the concentration of A, so:

[Math Processing Error]

Notice that the rate is proportional to the square of the concentration, so this is a second-order reaction.
Assume that the initial concentration of [A] is [A]*[Math Processing Error]*, and the initial concentration of [B] is zero.

1. Obtain an expression for [A]*[Math Processing Error]*.
2. Write down a mass balance (a relationship relating [A](t), [B](t), [A]*[Math Processing Error]* and [B]*[Math Processing Error]*) and obtain [B]*[Math Processing Error]*.
3. Using the definition of half-life *[Math Processing Error]*, obtain an expression for *[Math Processing Error]* for this mechanism. Your result will be a function of *[Math Processing Error]* and [A]*[Math Processing Error]*.

Problem *[Math Processing Error]*

Obtain *[Math Processing Error]* and*[Math Processing Error]* for the following mechanism:

[Math Processing Error]

Assume *[Math Processing Error]*, and *[Math Processing Error]*

Note that this problem is identical to the one solved in Section 4.2 but with *[Math Processing Error]*. Be sure you identify the step where the two problems become different.

Problem [Math Processing Error]

Consider the reaction

[Math Processing Error]

modeled mathematically by the following ODE

[Math Processing Error]

The constants, [Math Processing Error] and [Math Processing Error] represent the kinetic constants in the forward and backward direction respectively, and [A] and [B] represent the molar concentration of A and B. Assume you start with initial concentrations [Math Processing Error] and [Math Processing Error].

Mass conservation requires that [Math Processing Error]

1. Obtain [A](t) and [B](t) in terms of [Math Processing Error] and [Math Processing Error].
2. Obtain expressions for the concentrations of A and B in equilibrium: [Math Processing Error]) and [Math Processing Error]).
3. Prove that the equilibrium constant of the reaction, [Math Processing Error], can be expressed as [Math Processing Error]
4. Assume that [Math Processing Error], [Math Processing Error], [Math Processing Error] and [Math Processing Error], calculate [Math Processing Error] and [Math Processing Error], and sketch [Math Processing Error] and [Math Processing Error] to the best of your abilities.

CHAPTER OVERVIEW

5: Second Order Ordinary Differential Equations

Chapter Objectives

- Be able to obtain the general solution of any homogeneous second order ODE with constant coefficients.
- Be able to obtain particular solutions when initial conditions are given.
- Understand how to solve the equation of motion of a pendulum and a spring in non-viscous and viscous media.
- Understand how to solve the Schrödinger equation for the one dimensional particle in the box. Obtain the normalized eigenfunctions and the eigenvalues.

5.1: Second Order Ordinary Differential Equations

Solving second order ordinary differential equations is much more complex than solving first order ODEs. We just saw that there is a general method to solve any linear 1st order ODE. Unfortunately, this is not true for higher order ODEs. However, we can solve higher order ODEs if the coefficients are constants:

$$y''(x)+k_1y'(x)+k_2y(x)+k_3=0$$

The equation above is said to be homogeneous if $k_3=0$:

$$y''(x)+k_1y'(x)+k_2y(x)=0 \tag{5.1.1}$$

It is possible to solve non-homogeneous ODEs, but in this course we will concentrate on the homogeneous cases. Second order linear equations occur in many important applications. For example, the motion of a mass on a spring, and any other simple oscillating system, is described by an equation of the form

$$m\frac{d^2u}{dt^2}+\gamma\frac{du}{dt}+ku=F(t)$$

We'll analyze what the different parts of this equation mean in the examples. The equation above is homogeneous if $F(t)=0$.

Let's analyze Equation 5.1.1, which is linear and homogeneous. The parameters m, γ and k represent physical quantities that do not depend on the value of x, and therefore the equation has constant coefficients.This equation will be satisfied by a function whose derivatives are multiples of itself. This is the only way that we will get zero after adding a multiple of the function plus a multiple of its first derivative plus a multiple of the second derivative. You may be tempted to say that $\sin(x)$ satisfies this requirement, but its first derivative is $\cos x$, so it will not cancel out with the sine term when added together. The only functions that satisfy this requirement are the expnential functions $e^{\alpha x}$, with first and second derivatives $\alpha e^{\alpha x}$ and $\alpha^2e^{\alpha x}$ respectively. So, let's assume that the answer we are looking for is an exponential function, $y(x)=e^{\alpha x}$, and let's plug these expressions back into Equation 5.1.1:

$$\alpha^2e^{\alpha x}+k_1\alpha e^{\alpha x}+k_2e^{\alpha x}=0$$

$$e^{\alpha x}\left(\alpha^2+k_1\alpha+k_2\right)=0$$

Thee above equation tells us that either $e^{\alpha x}$ or $\left(\alpha^2+k_1\alpha+k_2\right)$ are zero. In the first case, this would mean that x is plus or minus infinity (depending on whether α is negative or positive). But this is too restrictive because we want to find a solution that is a function of x, so we don't want to impose restrictions on our independent variable. We therefore consider

$$\left(\alpha^2+k_1\alpha+k_2\right)=0$$

This is a quadratic equation in α, which we will call the auxiliary equation. The two roots are found from:

$$\alpha_{1,2}=\frac{-k_1\pm\sqrt{k_1^2-4k_2}}{2}$$

This gives two answers, α_1 and α_2, which means there are at least two different exponential functions that are solutions of the differential equation: e^{α_1x} and e^{α_2x}. We will see that any linear combination of these two functions is also a solution, but before continuing, let's look at a few examples. Notice that the argument of the square root can be positive, negative or zero, depending on the relative values of k_1 and k_2. This means that $\alpha_{1,2}$ can be imaginary, and the solutions can therefore be complex exponentials. Let's look at the three situations individually through examples.

Case I: $k_1^2-4k_2>0$

In this case, $\sqrt{k_1^2-4k_2}>0$, and therefore α_1 and α_2 are both real and different.

For example: Find the solution of $y''(x)-5y'(x)+4y(x)=0$ subject to initial conditions $y(0)=1$ and $y'(0)=-1$.

As we discussed above, we'll assume the solution is $y(x)=e^{\alpha x}$, and we'll determine which values of α satisfy this particular differential equation. Let's replace $y(x), y'(x)$ and $y''(x)$ in the differential equation:

$$\alpha^2 e^{\alpha x} - 5\alpha e^{\alpha x} + 4 e^{\alpha x} = 0$$

$$e^{\alpha x}\left(\alpha^2 - 5\alpha + 4\right) = 0$$

and with the arguments we discussed above:

$$\left(\alpha^2 - 5\alpha + 4\right) = 0$$

$$\alpha_{1,2} = \frac{-(-5) \pm \sqrt{(-5)^2 - 4 \times 4}}{2}$$

from which we obtain $\alpha_1 = 1$ and $\alpha_2 = 4$. Therefore, e^x and e^{4x} are both solutions to the differential equation. Let's prove this is true. If $y(x) = e^{4x}$, then $y'(x) = 4e^{4x}$ and $y''(x) = 16e^{4x}$. Substituting these expressions in the differential equation we get

$$y''(x) - 5y'(x) + 4y(x) = 16e^{4x} - 5 \times 4e^{4x} + 4 \times e^{4x} = 0$$

so $y(x) = e^{4x}$ clearly satisfies the differential equation. You can do the same with $y(x) = e^x$ and prove it is also a solution.

However, none of these solutions satisfy both initial conditions, so clearly we are not finished. We found two independent solutions to the differential equation, and now we will claim that any linear combination of these two independent solutions ($c_1 y_1(x) + c_2 y_2(x)$) is also a solution. Mathematically, this means that if $y_1(x)$ and $y_2(x)$ are solutions, then $c_1 y_1(x) + c_2 y_2(x)$ is also a solution, where c_1 and c_2 are constants (i.e. not functions of x). Coming back to our example, the claim is that $c_1 e^{4x} + c_2 e^x$ is the general solution of this differential equation. Let's see if it's true:

$$\begin{aligned} y(x) &= c_1 e^{4x} + c_2 e^x \\ y'(x) &= 4c_1 e^{4x} + c_2 e^x \\ y''(x) &= 16 c_1 e^{4x} + c_2 e^x \end{aligned}$$

Substituting in the differential equation:

$$y''(x) - 5y'(x) + 4y(x) = 16c_1 e^{4x} + c_2 e^x - 5 \times \left(4c_1 e^{4x} + c_2 e^x\right) + 4 \times \left(c_1 e^{4x} + c_2 e^x\right) = 0$$

so we just proved that the linear combination is also a solution, independently of the values of c_1 and c_2. It is important to notice that our general solution has now two arbitrary constants, as expected for a second order differential equation. We will determine these constants from the initial conditions to find the particular solution.

The general solution is $y(x) = c_1 e^{4x} + c_2 e^x$. Let's apply the first initial condition: $y(0) = 1$.

$$y(0) = c_1 + c_2 = 1$$

This gives a relationship between c_1 and c_2. The second initial condition is $y'(0) = -1$.

$$y'(x) = 4c_1 e^{4x} + c_2 e^x \rightarrow y'(0) = 4c_1 + c_2 = -1$$

We have two equations with two unknowns that we can solve to get $c_1 = -2/3$ and $c_2 = 5/3$.

The particular solution is then:

$$y(x) = -\frac{2}{3} e^{4x} + \frac{5}{3} e^x$$

Case II: $k_1^2 - 4k_2 < 0$

In this case, $k_1^2 - 4k_2 < 0$, so , $\sqrt{k_1^2 - 4k_2} = i\sqrt{-k_1^2 + 4k_2}$ where $\sqrt{-k_1^2 + 4k_2}$ is a real number. Therefore, in this case,

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2} = \frac{-k_1 \pm i\sqrt{-k_1^2 + 4k_2}}{2}$$

and then the two roots α_1 and α_2 are complex conjugates. Let's see how it works with an example.

Determine the solution of $y''(x) - 3y'(x) + \frac{9}{2} y(x) = 0$ subject to the initial conditions $y(0) = 1$ and $y'(0) = -1$.

Following the same methodology we discussed for the previous example, we assume $y(x) = e^{\alpha x}$, and use this expression in the differential equation to obtain a quadratic equation in α:

$$\alpha_{1,2} = \frac{3 \pm \sqrt{(-3)^2 - 4 \times 9/2}}{2} = \frac{3 \pm \sqrt{-9}}{2}$$

Therefore, $\alpha_1 = \frac{3}{2} + \frac{3}{2}i$ and $\alpha_2 = \frac{3}{2} - \frac{3}{2}i$, which are complex conjugates. The general solution is:

$$y(x) = c_1 e^{(\frac{3}{2} + \frac{3}{2}i)x} + c_2 e^{(\frac{3}{2} - \frac{3}{2}i)x}$$
$$y(x) = c_1 e^{\frac{3}{2}x} e^{\frac{3}{2}ix} + c_2 e^{\frac{3}{2}x} e^{-\frac{3}{2}ix}$$
$$y(x) = e^{\frac{3}{2}x} \left(c_1 e^{\frac{3}{2}ix} + c_2 e^{-\frac{3}{2}ix} \right)$$

This expression can be simplified using Euler's formula: $e^{\pm ix} = \cos(x) \pm i \sin x$ (Equation $2.2.1$).

$$y(x) = e^{\frac{3}{2}x} \left[c_1 \left(\cos(\frac{3}{2}x) + i \sin(\frac{3}{2}x) \right) + c_2 \left(\cos(\frac{3}{2}x) - i \sin(\frac{3}{2}x) \right) \right]$$

Grouping the sines and cosines together:

$$y(x) = e^{\frac{3}{2}x} \left[\cos(\frac{3}{2}x)(c_1 + c_2) + i \sin(\frac{3}{2}x)(c_1 - c_2) \right]$$

Renaming the constants $c_1 + c_2 = a$ and $i(c_1 - c_2) = b$

$$y(x) = e^{\frac{3}{2}x} \left[a \cos(\frac{3}{2}x) + b \sin(\frac{3}{2}x) \right]$$

Our general solution has two arbitrary constants, as expected from a second order ODE. As usual, we'll use our initial conditions to determine their values. The first initial condition is $y(0) = 1$

$$y(0) = a = 1 \quad (e^0 = 1, \cos(0) = 1 \quad \text{and} \quad \sin(0) = 0)$$

So far, we have

$$y(x) = e^{\frac{3}{2}x} \left[\cos(\frac{3}{2}x) + b \sin(\frac{3}{2}x) \right]$$

The second initial condition is $y'(0) = -1$

$$y'(x) = e^{\frac{3}{2}x} \left[-\sin(\frac{3}{2}x) + b \cos(\frac{3}{2}x) \right] \frac{3}{2} + \frac{3}{2} e^{\frac{3}{2}x} \left[\cos(\frac{3}{2}x) + b \sin(\frac{3}{2}x) \right]$$
$$y'(0) = \frac{3}{2}b + \frac{3}{2} = -1 \rightarrow b = -\frac{5}{3}$$

The particular solution is, therefore:

$$y(x) = e^{\frac{3}{2}x} \left[\cos(\frac{3}{2}x) - \frac{5}{3} \sin(\frac{3}{2}x) \right]$$

Notice that the function is real even when the roots were complex numbers.

Case III: $k_1^2 - 4k_2 = 0$

The last case we will analyze is when $k_1^2 - 4k_2 = 0$, which results in

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2} = \alpha_{1,2} = \frac{-k_1}{2}$$

Therefore, the two roots are real, and identical. This means that $e^{-k_1 x/2}$ is a solution, but this creates a problem because we need another independent solution to create the general solution from a linear combination, and we have only one. The second solution can be found using a method called reduction of order. We will not discuss the method in detail, although you can see how it is used in this case at the end of the video http://tinyurl.com/mpl69ju. The application of the method of reduction of order to this differential equation gives $(a+bx)e^{-k_1x/2}$ as the general solution. The constants a and b are arbitrary constants that we will determine from the initial/boundary conditions. Notice that the exponential term is the one we found using the 'standard' procedure. Let's see how it works with an example.

Determine the solution of $y''(x) - 8y'(x) + 16y(x) = 0$ subject to initial conditions $y(0) = 1$ and $y'(0) = -1$.

We follow the procedure of the previous examples and calculate the two roots:

$$\alpha_{1,2} = \frac{-k_1 \pm \sqrt{k_1^2 - 4k_2}}{2} = \frac{8 \pm \sqrt{8^2 - 4 \times 16}}{2} = 4$$

Therefore, e^{4x} is a solution, but we don't have another one to create the linear combination we need. The method of reduction of order gives:

$$y(x) = (a+bx)e^{4x}$$

Since we accepted the result of the method of reduction of order without seeing the derivation, let's at least show that this is in fact a solution. The first and second derivatives are:

$$y'(x) = be^{4x} + 4(a+bx)e^{4x}$$

$$y''(x) = 4be^{4x} + 4be^{4x} + 16(a+bx)e^{4x}$$

Substituting these expressions in $y''(x) - 8y'(x) + 16y(x) = 0$:

$$\left[4be^{4x} + 4be^{4x} + 16(a+bx)e^{4x}\right] - 8\left[be^{4x} + 4(a+bx)e^{4x}\right] + 16\left[(a+bx)e^{4x}\right] = 0$$

Because all these terms cancel out to give zero, the function $y(x) = (a+bx)e^{4x}$ is indeed a solution of the differential equation.

Coming back to our problem, we need to determine a and b from the initial conditions. Let's start with $y(0) = 1$:

$$y(0) = a = 1$$

So far, we have $y(x) = (1+bx)e^{4x}$, and therefore $y'(x) = be^{4x} + 4(1+bx)e^{4x}$. The other initial condition is $y'(0) = -1$:

$$y'(0) = b + 4 = -1 \rightarrow b = -5$$

The particular solution, therefore, is $y(x) = (1-5x)e^{4x}$

> This video contains an example of each of the three cases discussed above as well as the application of the method of reduction of order to case III. Remember that you can pause, rewind and fast forward so you can watch the videos at your own pace. http://tinyurl.com/mpl69ju

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5.2: Second Order Ordinary Differential Equations - Oscillations

Note

This section is also available in video format: http://tinyurl.com/kq7mrcq

The motion of a frictionless pendulum

We will now use what we learned so far to solve a problem of relevance in the physical sciences. We'll start with the problem of the pendulum, and as we already discussed in Section 3.2, even if the pendulum is not particularly interesting as an application in chemistry, the topic of oscillations is of great interest due to the fact that atoms in molecules vibrate around their bonds.

The problem of the pendulum was introduced in Figure 3.5, which is reprinted again below:

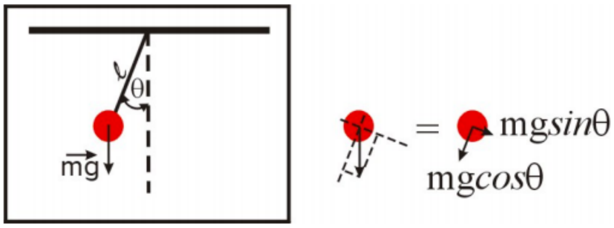


Figure 5.2.1: A rigid pendulum with massless and inextensible cord of length l. The motion is assumed to occur in two dimensions, and the friction is assumed to be negligible. The mass of the object is m, and g is the acceleration due to gravity. (CC BY-NC-SA; Marcia Levitus)

If you took a university physics course, you may recognize that Newton's second law yields:

$$ml\frac{d^2\theta}{dt^2}+mg\sin\theta=0 \tag{5.2.1}$$

This, unfortunately, is a non-linear differential equation (the dependent variable, θ, appears as the argument of a transcendental function). As we discussed in Section 3.2, this ODE has no analytical solution. It is possible to solve this equation numerically (and you will do it in the lab), but we cannot get an equation that is the solution of this ODE. We also discussed that we can obtain analytical solutions if we assume that the angle θ is small at all times. This means that the solution we get is valid only if the pendulum oscillates very close to the line normal to the ceiling. You may be thinking that studying such a system is boring and useless, but again, as we discussed in Section 3.2, for most molecules at moderate temperatures the displacement of the atoms around their equilibrium position is very small. That is why studying oscillations of systems close to equilibrium makes sense for a chemist.

We already discussed that if $\theta << 1$, then $\sin\theta \approx \theta$ (see Figure 3.4). Equation 5.2.1 can then be simplified to:

$$\frac{d^2\theta}{dt^2}+\frac{g}{l}\theta=0$$

This equation is linear in θ, is homogeneous, and has constant coefficients (g is the acceleration of gravity and l the length of the rod). The auxiliary equation of this ODE is:

$$\alpha^2+\frac{g}{l}=0$$

and therefore,

$$\alpha=\pm i\sqrt{\frac{g}{l}}$$

The general solution is

$$\theta(t)=c_1e^{\alpha_1 t}+c_2e^{\alpha_2 t}$$

$$\theta(t)=c_1e^{i(g/l)^{1/2}t}+c_2e^{-i(g/l)^{1/2}t}$$

We will get the values of the arbitrary constants from the initial conditions. Let's assume that at time zero the value of θ was $\theta_0 << 1$, and the value of $d\theta/dt$, which is a measure of the velocity, was $\theta'(0) = 0$. Physically, it means that at time zero we are holding the pendulum still. At this point we can either use Euler relationships to simplify our result into a cosine and a sine, or use the initial conditions and use Euler's relationship later. Either way will work, and how you choose to proceed is a matter of personal taste. Let's apply the initial conditions now:

$$\theta(t) = c_1 e^{i(g/l)^{1/2}t} + c_2 e^{-i(g/l)^{1/2}t} \rightarrow \theta(0) = c_1 + c_2 = \theta_0$$

$$\theta'(t) = c_1 i(g/l)^{1/2} e^{i(g/l)^{1/2}t} - c_2 i(g/l)^{1/2} e^{-i(g/l)^{1/2}t}$$

$$\theta'(0) = c_1 i(g/l)^{1/2} - c_2 i(g/l)^{1/2} = 0 \rightarrow c_1 = c_2$$

Therefore, $c_1 = c_2 = \theta_0/2$, and our particular solution is:

$$\theta(t) = \frac{\theta_0}{2}\left(e^{i(g/l)^{1/2}t} + e^{-i(g/l)^{1/2}t}\right)$$

From Euler's relationship we know that $e^{ix} + e^{-ix} = 2cosx$, so

$$\theta(t) = \theta_0 \cos\left(\left(\frac{g}{l}\right)^{1/2} t\right) \tag{5.2.2}$$

This is of course the familiar periodic function that you saw in your physics course. Remember that we got here by assuming $\theta << 1$ at all times.

As we saw in Section 1.4, the period of the function $\cos(nx)$ is $2\pi/n$. The period of the function $\theta_0 \cos\left(\left(\frac{g}{l}\right)^{1/2} t\right)$ is therefore $P = 2\pi\left(\frac{l}{g}\right)^{1/2}$. The period has units of time, and it tells us the time that it takes for the pendulum to complete a whole cycle (see Figure 5.2.2).

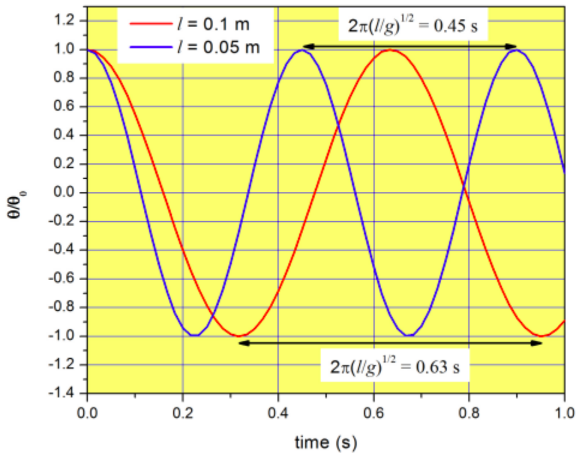


Figure 5.2.2: The oscillations of a pendulum in a frictionless medium (Equation 5.2.2). (CC BY-NC-SA; Marcia Levitus)

We can also calculate the frequency of the motion, which is just the reciprocal of the period. If the period is the amount of time you need to wait to complete a full cycle, the reciprocal is the number of cycles per unit time. For example, if it takes a pendulum with $l = 0.1m$ 0.63 seconds to complete a cycle, this means that we get 1.58 cycles per second. The frequency has units of reciprocal time.

The fact that pendula with different lengths have different periods was used by a very creative mind to produce the beautiful display showcased a the lobby of the PSF building at ASU (right across the elevators). There are some videos on YouTube demonstrating the idea (search for pendulum waves), but the one in the physics department at ASU is much more impressive, so go and check it out if you haven't done so yet.

The pendulum in a viscous medium

The problem we just saw assumed that there was no friction, so the pendulum will oscillate forever without changing the amplitude. Let's make the problem more realistic from the physical point of view and add a term that accounts for frictional resistance. The force due to friction is usually proportional to the velocity, so this new force introduces a term that depends on the first derivative of θ:

$$\frac{d^2\theta}{dt^2}+\gamma\frac{d\theta}{dt}+\frac{g}{l}\theta=0$$

The constant γ depends on the medium, and it will be larger in e.g. water (more friction) than in air (less friction). The auxiliary equation is now

$$\alpha^2+\gamma\alpha+\frac{g}{l}=0$$

and the two roots are:

$$\alpha_{1,2}=\frac{-\gamma\pm\sqrt{\gamma^2-4g/l}}{2}$$

and we see that the result will depend on the relative values of γ^2 and $4g/l$. We will analyze the case $\gamma^2<4g/l$ first (low friction regime). It is useful to always think about what one expects before doing any math. Think about the pendulum without friction, and imagine you do the same experiment in air (small friction). How do you think the plot of $\theta(t)$ vs t would look like?

Coming back to the math, let's call $a=\sqrt{4g/l-\gamma^2}$ to simplify notation. In the low friction case, a will be a real number. The two roots will therefore be:

$$\alpha_{1,2}=\frac{-\gamma\pm ia}{2}$$

and the general solution will be

$$\theta(t)=c_1e^{\alpha_1 t}+c_1e^{\alpha_2 t}$$

$$\theta(t)=c_1e^{-\gamma t/2}e^{iat/2}+c_2e^{-\gamma t/2}e^{-iat/2}$$

$$\theta(t)=e^{-\gamma t/2}\left(c_1e^{iat/2}+c_2e^{-iat/2}\right)$$

At this point we can either use the initial conditions and use Euler's relationship later, or we can use Euler's equations now and the initial conditions later. Either way should work.

$$\theta(t)=e^{-\gamma t/2}\left[\left(c_1\cos(ta/2)+c_1 i\sin(ta/2)+c_2\cos(ta/2)-c_2 i\sin(ta/2)\right)\right]$$

$$\theta(t)=e^{-\gamma t/2}\left[(c_1+c_2)\cos(ta/2)+(c_1-c_2)i\sin(ta/2)\right]$$

and grouping and re-naming constants:

$$\theta(t)=e^{-\gamma t/2}\left[c_3\cos(ta/2)+c_4\sin(ta/2)\right]$$

We will now evaluate c_3 and c_4 from the initial conditions. Let's assume again that $\theta(0)=\theta_0$ and $\theta'(0)=0$. Evaluating the previous equation at $t=0$:

$$\theta(0)=c_3=\theta_0$$

so we have

$$\theta(t)=e^{-\gamma t/2}\left[\theta_0\cos\left(\frac{ta}{2}\right)+c_4\sin\left(\frac{ta}{2}\right)\right]$$

$$\theta'(t)=e^{-\gamma t/2}\left[-\frac{\theta_0 a}{2}\sin\left(\frac{ta}{2}\right)+\frac{c_4 a}{2}\cos\left(\frac{ta}{2}\right)\right]-\frac{\gamma}{2}e^{-\gamma t/2}\left[\theta_0\cos\left(\frac{ta}{2}\right)+c_4\sin\left(\frac{ta}{2}\right)\right]$$

$$\theta'(0)=c_4\frac{a}{2}-\theta_0\frac{\gamma}{2}=0$$

$$c_4 = \frac{\gamma\theta_0}{a}$$

and therefore

$$\theta(t) = e^{-\gamma t/2}\left[\theta_0 \cos\left(\frac{ta}{2}\right) + \frac{\gamma\theta_0}{a}\sin\left(\frac{ta}{2}\right)\right]$$

$$\theta(t) = \theta_0 e^{-\gamma t/2}\left[\cos\left(\frac{ta}{2}\right) + \frac{\gamma}{a}\sin\left(\frac{ta}{2}\right)\right]$$

If everything went well this equation should simplify to Equation 5.2.2 for the case $\gamma = 0$. Recall that $a = \sqrt{4g/l - \gamma^2}$, so if $\gamma = 0$:

$$\theta(t) = \theta_0\left[\cos\left(\frac{ta}{2}\right)\right]$$

$$\theta(t) = \theta_0\left[\cos\left(\sqrt{\frac{g}{l}}t\right)\right]$$

This of course does not prove that our solution is correct, but it is always good to see that we recover a known equation for a particular case (in this case $\gamma = 0$).

Figure $5.2.3$ shows $\theta(t)/\theta_0$ for three cases with $g/l = 1$ (i.e. a cord of length 9.8 m) and increasing values of friction. Remember that we are assuming that θ is small.

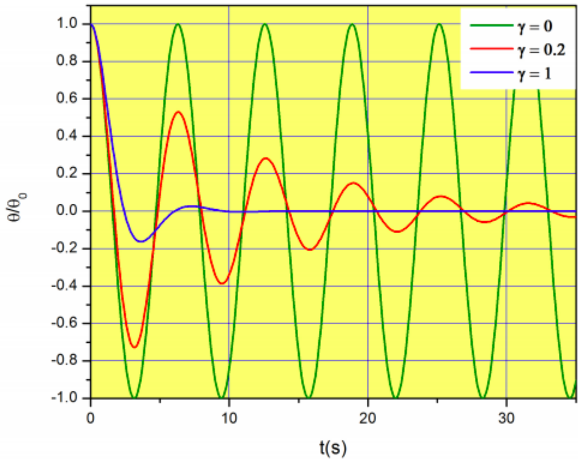


Figure $5.2.3$: A pendulum in low-friction media (l = 9.8m) (CC BY-NC-SA; Marcia Levitus)

So far we have analyzed the case $\gamma^2 < 4g/l$. As we increase the friction coefficient, we will reach the point where $\gamma^2 = 4g/l$. Look at Figure $5.2.3$, and think about what you would see when this happens. Mathematically, we will have two repeated roots:

$$\alpha_{1,2} = \frac{-\gamma \pm \sqrt{\gamma^2 - 4g/l}}{2} = -\frac{\gamma}{2}$$

so $\theta(t) = e^{-\gamma t/2}$ is a solution, but we need to find an independent solution through the method of reduction of order. We know that the general solution will be (Section 2.2):

$$\theta(t) = (c_1 + c_2 t)e^{-\gamma t/2}$$

The arbitrary constants will be calculated from the initial conditions:

$$\theta(0) = (c_1) = \theta_0$$

$$\theta'(t) = -\frac{\gamma}{2}(\theta_0 + c_2 t)e^{-\gamma t/2} + c_2 e^{-\gamma t/2}$$

$$\theta'(0) = -\frac{\gamma}{2}(\theta_0) + c_2 = 0$$

$$c_2 = \frac{\gamma}{2}\theta_0$$

Therefore,

$$\theta(t) = (c_1 + c_2 t)e^{-\gamma t/2}$$

$$\theta(t) = (\theta_0 + \frac{\theta_0 \gamma}{2} t)e^{-\gamma t/2} = \theta_0 (1 + \frac{\gamma}{2} t)e^{-\gamma t/2}$$

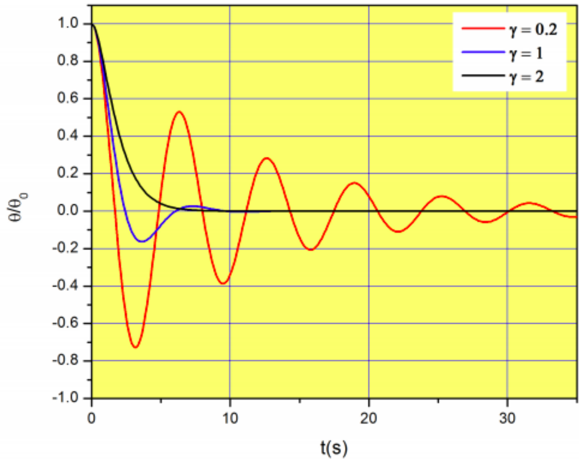


Figure 5.2.4: A critically damped pendulum with l = 9.8m (black) (CC BY-NC-SA; Marcia Levitus)

The behavior of $\theta(t)$ is shown in Figure 5.2.4 in black. This regime is called critically damped because it represents the point where the oscillations no longer occur as γ increases. If we continue increasing the frictional coefficient, the pendulum will approach $\theta = 0$ slower and slower, but will never cross to the other side ($\theta < 0$). Let's find the mathematical expression for $\theta(t)$ for the case $\gamma^2 > 4g/l$. The two roots are now different and real:

$$\alpha_{1,2} = \frac{-\gamma \pm \sqrt{\gamma^2 - 4g/l}}{2}$$

and the general solution is therefore

$$\theta(t) = c_1 e^{\alpha_1 t} + c_2 e^{\alpha_2 t}$$

$$\theta(t) = c_1 e^{(-\gamma+b)t/2} + c_2 e^{(-\gamma-b)t/2}; \; b = \sqrt{\gamma^2 - 4g/l}$$

The first initial condition is $\theta(0) = \theta_0$:

$$\theta(0) = c_1 + c_2 = \theta_0$$

The second initial condition is $\theta'(t) = 0$:

$$\theta'(t) = c_1 \left(\frac{-\gamma + b}{2}\right) e^{(-\gamma+b)t/2} + c_2 \left(\frac{-\gamma - b}{2}\right) e^{(-\gamma-b)t/2}$$

$$\theta'(0) = c_1 \left(\frac{-\gamma + b}{2}\right) + c_2 \left(\frac{-\gamma - b}{2}\right) = 0$$

$$\theta'(0) = -(c_1 + c_2)\gamma + (c_1 - c_2)b = 0$$

the first initial condition yielded $c_1 + c_2 = \theta_0$ so

$$\theta'(0) = -\theta_0 \gamma + (c_1 - c_2)b = 0$$

$$(c_1 - c_2) = \theta_0 \gamma / b$$

The two initial conditions gave two relationships between c_1 and c_2:

$$c_1 + c_2 = \theta_0$$

$$(c_1 - c_2) = \theta_0 \gamma / b$$

Solving this system of two equations with two unknowns:

$$c_1 = \frac{\theta_0}{2}\left(1 + \frac{\gamma}{b}\right)$$

$$c_2 = \frac{\theta_0}{2}\left(1 - \frac{\gamma}{b}\right)$$

And finally we can write the particular solution as:

$$\theta(t) = c_1 e^{(-\gamma+b)t/2} + c_2 e^{(-\gamma-b)t/2};\ b = \sqrt{\gamma^2 - 4g/l}$$

$$\theta(t) = \frac{\theta_0}{2}\left(1 + \frac{\gamma}{b}\right) e^{(-\gamma+b)t/2} + \frac{\theta_0}{2}\left(1 - \frac{\gamma}{b}\right) e^{(-\gamma-b)t/2};\ b = \sqrt{\gamma^2 - 4g/l}$$

$$\theta(t) = \frac{\theta_0}{2} e^{-\gamma t/2}\left[\left(1 + \frac{\gamma}{b}\right) e^{bt/2} + \left(1 - \frac{\gamma}{b}\right) e^{-bt/2}\right]$$

Figure $5.2.5$ shows results with $g/l = 1$, and three different values of γ. Notice that $\gamma = 2$ corresponds to the critically damped regime.

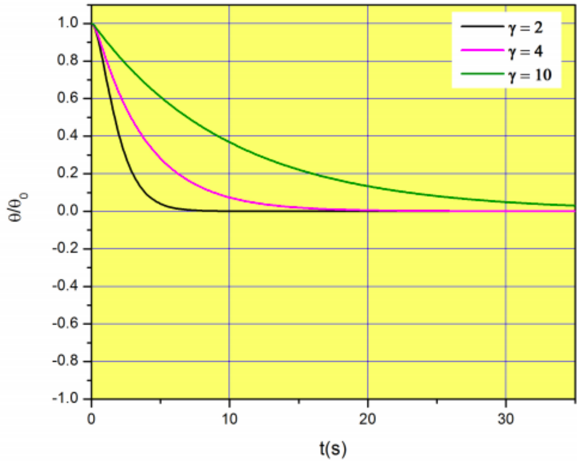


Figure $5.2.5$: The high friction regime ($\gamma^2 > 4g/l$) (CC BY-NC-SA; Marcia Levitus)

5.3: Second Order Ordinary Differential Equations with Boundary Conditions

Note

This section is also available in video format: http://tinyurl.com/n8tgbf6

You may have noticed that all the examples we discussed so far in this chapter involve initial conditions, or in other words, conditions evaluated at the same value of the independent value. We will see now how boundary conditions give rise to important consequences in the solutions of differential equations, which are extremely important in the description of atomic and molecular systems. Let's start by asking ourselves whether all boundary value problems involving homogeneous second order ODEs have non-trivial solutions. The trivial solution is $y(x)=0$, which is a solution to any homogeneous ODE, but this solution is not particularly interesting from the physical point of view. For example, let's solve the following problem:

$$y''(x)+3y(x)=0;\ y('0)=0;\ y(1)=0$$

Following the same procedure we have used in previous examples, we get the following general solution:

$$y(x)=a\cos(\sqrt{3}x)+b\sin(\sqrt{3}x)$$

The first boundary condition is $y'(0)=0$:

$$y'(x)=-\sqrt{3}a\sin(\sqrt{3}x)+\sqrt{3}b\cos(\sqrt{3}x)\rightarrow y'(0)=\sqrt{3}b=0\rightarrow b=0$$

Therefore, so far we have $y(x)=a\cos(\sqrt{3}x)$. The second boundary condition is $y(1)=0$, so

$$y(1)=a\cos\sqrt{3}=0\rightarrow a=0$$

Therefore, the only particular solution for these particular boundary conditions is $y(x)=0$, the trivial solution. Let's change the question and ask ourselves now if there is any number λ, so that the equation

$$y''(x)+\lambda y(x)=0;\ y'(0)=0;\ y(1)=0$$

has a non-trivial solution. Our general solution depends on whether λ is positive or negative. If $\lambda>0$ we have

$$y(x)=a\cos(\sqrt{\lambda}x)+b\sin(\sqrt{\lambda}x)$$

Notice that we are using results be obtained in previous sections, but you would need to show all your work!

If $\lambda<0$ we have

$$y(x)=ae^{\sqrt{|\lambda|}x}+be^{-\sqrt{|\lambda|}x}$$

where $|\lambda|$ is the absolute value of λ.

Let's look at the case $\lambda<0$ first. The first boundary condition implies

$$y'(x)=\sqrt{|\lambda|}ae^{\sqrt{|\lambda|}x}-\sqrt{|\lambda|}be^{-\sqrt{|\lambda|}x}\rightarrow y'(0)=\sqrt{|\lambda|}(a-b)=0\rightarrow a=b$$

and therefore $y(x)=a\left(e^{\sqrt{|\lambda|}x}+e^{-\sqrt{|\lambda|}x}\right)$. Using the second boundary condition:

$$y(1)=a\left(e^{\sqrt{|\lambda|}}+e^{-\sqrt{|\lambda|}}\right)=0\rightarrow a=0$$

Therefore, if $\lambda<0$, the solution is always $y(x)=0$, the trivial solution.

Let's see what happens if $\lambda>0$. The general solution is $y(x)=a\cos(\sqrt{\lambda}x)+b\sin(\sqrt{\lambda}x)$, and applying the first boundary condition:

$$y'(x)=-\sqrt{\lambda}a\sin(\sqrt{\lambda}x)+\sqrt{\lambda}b\cos(\sqrt{\lambda}x)\rightarrow y'(0)=\sqrt{\lambda}b=0\rightarrow b=0$$

Therefore, so far we have $y(x)=a\cos\sqrt{\lambda}x$. The second boundary condition is $y(1)=0$, so

$$y(1)=a\cos(\sqrt{\lambda})=0$$

As before, $a = 0$ is certainly a possibility, but this again would give the trivial solution, which we are trying to avoid. However, this is not our only option, because there are some values of λ that also make $y(1) = 0$. These are $\sqrt{\lambda} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$, or in terms of λ:

$$\lambda = \frac{\pi^2}{4}, \frac{9\pi^2}{4}, \frac{25\pi^2}{4}$$

This means that

$$y''(x) + 3y(x) = 0;\ y'(0) = 0;\ y(1) = 0$$

does not have a non-trivial solution, but

$$y''(x) + (\pi^2/4)y(x) = 0;\ y'(0) = 0;\ y(1) = 0$$

does. The values of λ that guarantee that the differential equation has non-trivial solutions are called the **eigenvalues** of the equation. The non-trivial solutions are called the **eigenfunctions** of the equation. We just found the eigenvalues, but what about the eigenfunctions?

We just concluded that the solutions are $y(x) = a \cos \sqrt{\lambda} x$, and now we know that $\sqrt{\lambda} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}$. We can write the eigenfunctions as:

$$y(x) = a \cos \frac{(2n-1)\pi}{2} x \quad n = 1, 2, 3 \ldots$$

We could also use $(2n+1)$ with $n = 0, 1, 2 \ldots$. Notice that we do not have any information that allows us to calculate the constant a, so we leave it as an arbitrary constant.

Also, notice that although we have infinite eigenvalues, the eigenvalues are discrete. The term discrete means that the variable can take values for a countable set (like the natural numbers). The opposite of discrete is continuous (like the real numbers). These discrete eigenvalues have very important consequences in quantum mechanics. In fact, you probably know from your introductory chemistry classes that atoms and molecules have energy levels that are discrete. Electrons can occupy one orbital or the next, but cannot be in between. These energies are the eigenvalues of differential equations with boundary conditions, so this is an amazing example of what boundary conditions can do!

5.4: An example in Quantum Mechanics

The main postulate of quantum mechanics establishes that the state of a quantum mechanical system is specified by a function called *the wave function*. The wave function is a function of the coordinates of the particle (the position) and time. We often deal with *stationary states*, i.e. states whose energy does not depend on time. For example, at room temperature and in the absence of electromagnetic radiation such as UV light, the energy of the only electron in the hydrogen atom is constant (the energy of the 1s orbital). In this case, all the information about the state of the particle is contained in a time-independent function, $\psi(\mathbf{r})$, where $\mathbf{r}$ is a vector that defines the position of the particle. In Section 2.3 we briefly mentioned that $|\psi|^2 = \psi^*\psi$ can be interpreted in terms of the probability of finding the electron in different regions of space. Because the probability of finding the particle somewhere in the universe is 1, the wave function needs to be normalized (that is, the integral of $|\psi|^2$ over all space has to equal 1).

The fundamental equation in quantum mechanics is known as the Schrödinger equation, which is a differential equation whose solutions are the wave functions. For a particle of mass m moving in one dimension in a potential field described by $U(x)$ the Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=E\psi(x)$$

Notice that the position of the particle is defined by x, because we are assuming one-dimensional movement. The constant $\hbar$ (pronounced “h-bar”) is defined as $h/(2\pi)$, where h is Plank’s constant. $U(x)$ is the potential energy the particle is subjected to, and depends on the forces involved in the system. For example, if we were analyzing the hydrogen atom, the potential energy would be due to the force of interaction between the proton (positively charged) and the electron (negatively charged), which depends on their distance. The constant E is the total energy, equal to the sum of the potential and kinetic energies.

This will be confusing until we start seeing a few examples, so don’t get discouraged and be patient. Let’s start by discussing the simplest (from the mathematical point of view) quantum mechanical system. Our system consists of a particle of mass m that can move freely in one dimension between two “walls”. The walls are impenetrable, and therefore the probability that you find the particle outside this one-dimensional box is zero. This is not too different from a ping-pong ball bouncing inside a room. It does not matter how hard you bounce the ball against the wall, you will never find it on the other side. However, we will see that for microscopic particles (small mass), the system behaves very different than for macroscopic particles (the ping-pong ball). The behavior of macroscopic systems is described by the laws of what we call classical mechanics, while the behavior of molecules, atoms and sub-atomic particles is described by the laws of quantum mechanics. The problem we just described is known as the “particle in the box” problem, and can be extended to more dimensions (e.g. the particle can move in a 3D box) or geometries (e.g. the particle can move on the surface of a sphere, or inside the area of a circle).

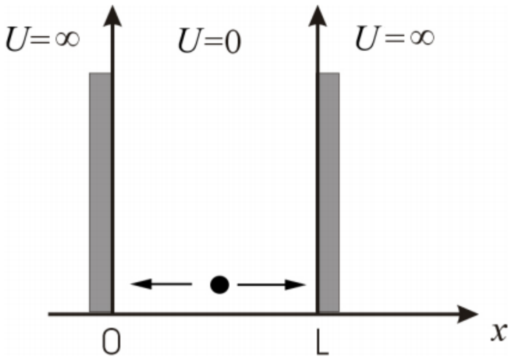


Figure 5.4.1: The problem of a particle in a one-dimensional box (CC BY-NC-SA; Marcia Levitus)

The particle in a one-dimensional box

We will start with the simplest case, which is a problem known as ’the particle in a one-dimensional box’ (Figure 5.4.1). This is a simple physical problem that, as we will see, provides a rudimentary description of conjugated linear molecules. In this problem, the particle is allowed to move freely in one dimension inside a ’box’ of length L. In this context, ’freely’ means that the particle is not subject to any force, so the potential energy inside the box is zero. The particle is not allowed to move outside the box, and physically, we guarantee this is true by impossing an infinite potential energy at the edges of the box ($x=0$ and $x=L$) and outside the box ($x<0$ and $x>L$).

$$U(x)=\begin{cases}\infty & x<0\\ 0 & 0<x<L\\ \infty & x>L\end{cases}$$

Because the potential energy outside the box is infinity, the probability of finding the particle in these regions is zero. This means that $\psi(x)=0$ if $x>L$ or $x<0$. What about $\psi(x)$ inside the box? In order to find the wave functions that describe the states of a system, we have to solve Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=E\psi(x)$$

Inside the box $U(x)=0$, so:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x)$$

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+E\psi(x)=0 \tag{5.4.1}$$

Remember that $\hbar$ is a constant, m is the mass of the particle (also constant), and E the energy. The energy of the particle is a constant in the sense that it is not a function of x. We will see that there are many (in fact infinite) possible values for the energy of the particle, but these are numbers, not functions of x. With all this in mind, hopefully you will recognize that the Schrödinger equation for the one-dimensional particle in a box is a homogeneous second order ODE with constant coefficients. Do we have any initial or boundary conditions? In fact we do, because the wave function needs to be a continuous function of x. This means that there cannot be sudden jumps of probability density when moving though space. In particular in this case, it means that $\psi(0)=\psi(L)=0$, because the probability of finding the particle outside the box is zero.

Let's solve Equation 5.4.1. We need to find the functions $\psi(x)$ that satisfy the ODE. The auxiliary equation is (remember that $m,\hbar,E$ are positive constants):

$$\frac{\hbar^2}{2m}\alpha^2+E=0$$

$$\alpha=\pm i\sqrt{\frac{2mE}{\hbar^2}}$$

and the general solution is therefore:

$$\psi(x)=c_1e^{i\sqrt{\frac{2mE}{\hbar^2}}x}+c_2e^{-i\sqrt{\frac{2mE}{\hbar^2}}x}$$

Because $\psi(0)=0$:

$$\psi(x)=c_1+c_2=0\rightarrow c_1=-c_2$$

$$\psi(x)=c_1\left(e^{i\sqrt{\frac{2mE}{\hbar^2}}x}-e^{-i\sqrt{\frac{2mE}{\hbar^2}}x}\right)$$

This can be simplified using Euler's relationships: $e^{ix}-e^{-ix}=2i\sin x$

$$\psi(x)=c_1(2i)\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

$$\psi(x)=A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}x\right)$$

In the last step we recognized that $2ic_1$ is a constant, and called it A.

The second boundary condition is $\psi(L)=0$:

$$\psi(L)=A\sin\left(\sqrt{\frac{2mE}{\hbar^2}}L\right)=0$$

We can make $A=0$, but this will result in the wave function being zero at all values of x. This is what we called the 'trivial solution' before, and although it is a solution from the mathematical point of view, it is not when we think about the physics of the problem. If $\psi(x)=0$ the probability of finding the particle inside the box is zero. However, the problem states that the particle cannot be found outside, so it has to be found inside with a probability of 1. This means that $\psi(x)=0$ is not a physically acceptable solution inside the box, and we are forced to consider the situations where

$$\sin\left(\sqrt{\frac{2mE}{\hbar^2}}L\right)=0$$

We know the function $\sin x$ is zero at values of x that are zero, or multiples of π:

$$\left(\sqrt{\frac{2mE}{\hbar^2}}L\right)=\pi,2\pi,3\pi\ldots=n\pi\;(n=1,2,3..\infty)$$

This means that our solution is:

$$\psi(x)=A\sin\left(\frac{n\pi}{L}x\right)\;(n=1,2,3\ldots\infty)$$

Notice that we didn't consider $n=0$ because that would again cause $\psi(x)$ to vanish inside the box. The functions $\psi(x)$ contain information about the state of the system, and are called the *eigenfunctions*. What about the energies?

$$\left(\sqrt{\frac{2mE}{\hbar^2}}L\right)=n\pi\rightarrow E=\left(\frac{n\pi}{L}\right)^2\frac{\hbar^2}{2m}\;(n=1,2,3\ldots\infty)$$

The energies are the *eigenvalues* of this equation. Notice that there are infinite eigenfunctions, and each one has a defined eigenvalue.

n	$\psi(x)$	E
1	$A\sin\left(\frac{\pi}{L}x\right)$	$\left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}$
2	$A\sin\left(\frac{2\pi}{L}x\right)$	$\left(\frac{2\pi}{L}\right)^2\frac{\hbar^2}{2m}$
3	$A\sin\left(\frac{3\pi}{L}x\right)$	$\left(\frac{3\pi}{L}\right)^2\frac{\hbar^2}{2m}$

The lowest energy state is described by the wave function $\psi=A\sin\left(\frac{\pi}{L}x\right)$, and its energy is $\left(\frac{\pi}{L}\right)^2\frac{\hbar^2}{2m}$.

What about the constant A? Mathematically, any value would work, and none of the boundary conditions impose any restriction on its value. Physically, however, we have another restriction we haven't fulfilled yet: the wave function needs to be normalized. The integral of $|\psi|^2$ over all space needs to be 1 because this function represents a probability.

$$\int_{-\infty}^{\infty}|\psi(x)|^2dx=1$$

However, $\psi(x)=0$ outside the box, so the ranges $x<0$ and $x>L$ do not contribute to the integral. Therefore:

$$\int_0^L|\psi(x)|^2dx=\int_0^L A^2\sin^2\left(\frac{n\pi}{L}x\right)dx=1$$

We will calculate A from this normalization condition. Using the primitives found in the formula sheet, we get:

$$\int_0^L\sin^2\left(\frac{n\pi}{L}x\right)dx=L/2$$

and therefore

$$A=\sqrt{\frac{2}{L}}$$

We can now write down our normalized wave function as:

$$\psi(x)=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)\ (n=1,2,3\ldots\infty)$$

We solved our first problem in quantum mechanics! Let's discuss what we got, and what it means. First, because the potential energy inside the box is zero, the total energy equals the kinetic energy of the particle (i.e. the energy due to the fact that the particle is moving from left to right or from right to left). A ping-pong ball inside a macroscopic box can move at any speed we want, so its kinetic energy is not quantized. However, if the particle is an electron, its kinetic energy inside the box can adopt only quantized values of energy: $E=\left(\frac{n\pi}{L}\right)^2\frac{\hbar^2}{2m}\ (n=1,2,3\ldots\infty)$. Interestingly, the particle cannot have zero energy ($n=0$ is not an option), so it cannot be at rest (our ping-pong ball can have zero kinetic energy without violating any physical law). If a ping-pong ball moves freely inside the box we can find it with equal probability close to the edges or close to the center. Not for an electron in a one-dimensional box! The function $|\psi(x)|^2$ for the lowest energy state ($n=1$) is plotted in Figure $5.4.2$. The probability of finding the electron is greater at the center than it is at the edges; nothing like what we expect for a macroscopic system. The plot is symmetric around the center of the box, meaning the probability of finding the particle in the left side is the same as finding it in the right side. That is good news, because the problem is truly symmetric, and there are no extra forces attracting or repelling the particle on the left or right half to the box.

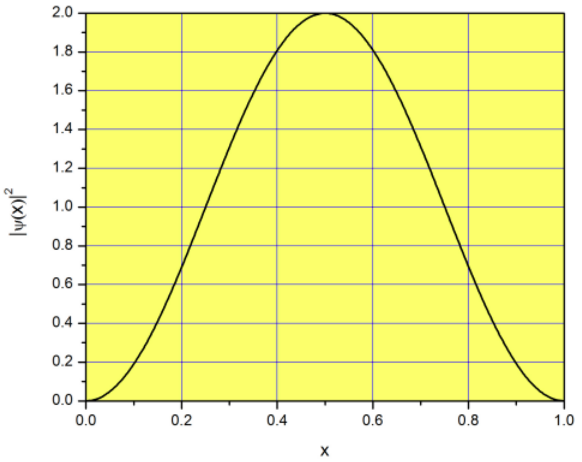


Figure $5.4.2$: The lowest energy state of a particle in a one-dimensional box of length $L=1$ (CC BY-NC-SA; Marcia Levitus)

Looking at Figure $5.4.2$, you may think that the probability of finding the particle at the center really 2. How can this be? Probabilities cannot be greater than 1! This is a major source of confusion among students, so let's clarify what it means. The function $|\psi(x)|^2$ is not a probability, but a probability density. Technically, this means that $|\psi(x)|^2dx$ is the probability of finding the particle between x and $x+dx$ (see page for more details). For example, the probability of finding the particle between $x=0.5$ and 0.5001 is $\approx|\psi(0.5)|^2\times 0.0001=0.0002$. This is approximate because $\Delta x=0.0001$ is small, but not infinitesimal. What about the probability of finding the particle between $x=0.5$ and 0.6? We need to integrate $|\psi(x)|^2dx$ between $x=0.5$ and $x=0.6$:

$$p(0.5<x<0.6)=\int_{0.5}^{0.6}|\psi(x)|^2dx\approx 0.2$$

Importantly,

$$p(0<x<1)=\int_{0}^{1}|\psi(x)|^2dx=1$$

as it should be the case for a normalized wave function. Notice that these probabilities refer to the lowest energy state ($n=1$), and will be different for states of increasing energy.

> The particle in the box problem is also available in video format: http://tinyurl.com/mjsmd2a

Where is the chemistry?

So far we talked about a system that sounds pretty far removed from anything we (chemists) care about. We understand electrons in atoms, but electrons moving in a one-dimensional box? To see why this is not such a crazy idea, let's consider the molecule of carotene (the orange pigment in carrots). We know that all those double bonds are conjugated, meaning that the π electrons are delocalized and relatively free to move around the bonds highlighted in red in Figure $5.4.3$.

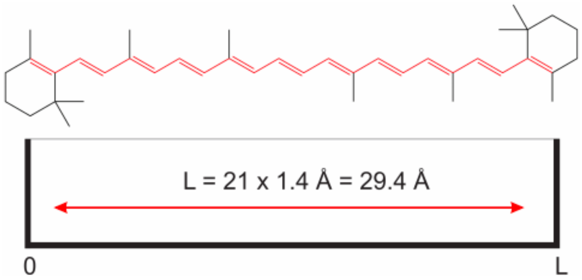


Figure $5.4.3$: The particle in a box model applied to carotene. (CC BY-NC-SA; Marcia Levitus)

Because the length of each carbon-carbon bond is around 1.4 $\mathring{A}$ ($\mathring{A}$ stands for angstrom, and equals $10^{-10}m$), we can assume that the π electrons move inside a one dimensional box of length $L = 21 \times 1.4$ Å$= 29.4$Å. This is obviously an approximation, as it is not true that the electrons move freely without being subject to any force. Yet, we will see that this simple model gives a good semi-quantitative description of the system.

We already solved the problem of the particle in a box, and obtained the following eigenvalues:

$$E = \left(\frac{n\pi}{L}\right)^2 \frac{\hbar^2}{2m} \; (n = 1, 2, 3 \ldots \infty) \tag{5.4.2}$$

These are the energies that the particle in the box is allowed to have. In this case, the particle in question is an electron, so m is the mass of an electron. Notice that we have everything we need to use Equation 5.4.2: $\hbar = 1.0545 \times 10^{-34} m^2 kg\, s^{-1}$, $m = 9.109 \times 10^{-31} kg$, and $L = 2.94 \times 10^{-9} m$. This will allow us to calculate the allowed energies for the π electrons in carotene. For $n = 1$ (the lowest energy state), we have:

$$E_1 = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m} = 6.97 \times 10^{-21} J$$

Joule is the unit of energy, and $1 J = kg \times m^2 \times s^{-2}$. A very easy way of remembering this is to recall Einstein's equation: $E = mc^2$, which tells you that energy is a mass times the square of a velocity (hence, $1J = 1kg(1m/s)^2$). Coming back to Equation 5.4.2, the allowed energies for the π electrons in carotene are:

$$E_n = n^2 \times 6.97 \times 10^{-21} J \; (n = 1, 2, 3 \ldots \infty)$$

Notice that the energies increase rapidly. The energy of the tenth level (E_{10}) is one hundred times the energy of the first! The number of levels is inifinite, but of course we know that the electrons will fill the ones that are lower in energy. This is analogous to the hydrogen atom. We know there are an infinite number of energy levels, but in the absence of an external energy source we know the electron will be in the 1s orbital, which is the lowest energy level. This electron has an infinite number of levels available, but we need an external source of energy if we want the electron to occupy a higher energy state. The same concepts apply to molecules. As you have learned in general chemistry, we cannot have more than two electrons in a given level, so we will put our 22 π electrons (2 per double bond) in the first 11 levels (Figure $5.4.4$, left).

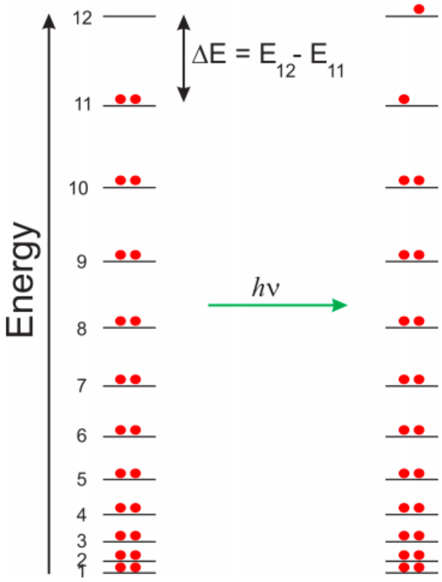


Figure 5.4.4: The particle in a box model applied to carotene (CC BY-NC-SA; Marcia Levitus)

We can promote an electron to the first unoccupied level (in this case $n = 12$) by using light of the appropriate frequency (ν). The energy of a photon is $E = h\nu$, where h is Plank's constant. In order for the molecule to absorb light, the wavelength of the light beam needs to match exactly the gap in energy between the highest occupied state (in this case $n = 11$) and the lowest unoccupied state. The wavelength of light is related to the frequency as: $\lambda = c/\nu$, where c is the speed of light. Therefore, in order to produce the excited state shown in the right side of Figure $5.4.4$, we have to use light of the following wavelength:

$$E = E_{12} - E_{11} = h\nu = hc/\lambda \rightarrow \lambda = hc/(E_{12} - E_{11})$$

Recall that $E_n = n^2 \times 6.97 \times 10^{-21} J$, so $(E_{12} - E_{11}) = (144 - 121) \times 6.97 \times 10^{-21} J = 1.60 \times 10^{-19} J$. Therefore,

$$\lambda = \frac{6.626 \times 10^{-34} J\, s \times 3 \times 10^{8} m\, s^{-1}}{1.60 \times 10^{-19} J} = 1.24 \times 10^{-6} m = 1,242 nm$$

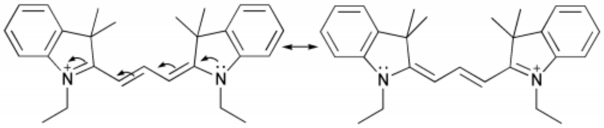
In the last step we expressed the result in nanometers ($1 nm = 10^{-9} m$), which is a common unit to describe the wavelength of light in the visible and ultraviolet regions of the electromagnetic spectrum. It is actually fairly easy to measure the absorption spectrum of carotene. You just need to have a solution of carotene, shine the solution with light of different colors (wavelengths), and see what percentage of the light is transmitted. The light that is not transmitted is absorbed by the molecules due to transitions such as the one shown in Figure $5.4.4$. In reality, the absorption of carotene actually occurs at 497 nm, not at 1,242 nm. The discrepancy is due to the huge approximations of the particle in the box model. Electrons are subject to interactions with other electrons, and with the nuclei of the atoms, so it is not true that the potential energy is zero. Although the difference seems large, you should not be too disappointed about the result. It is actually pretty impressive that such a simple model can give a prediction that is not that far from the experimental result. Nowadays chemists use computers to analyze more sophisticated models that cannot be solved analytically in the way we just solved the particle in the box. Yet, there are some qualitative aspects of the particle in the box model that are useful despite the approximations. One of these aspects is that the wavelength of the absorbed light gets lower as we reduce the size of the box. From Equation 5.4.2, we can write:

$$hc/\lambda = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}(n_2^2 - n_1^2)$$

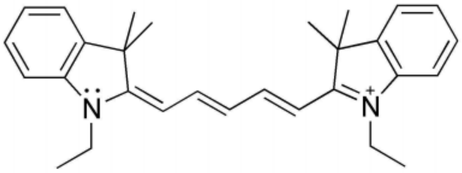
where n_2 is the lowest unoccupied level, and n_1 is the highest occupied level. Because $n_2 = n_1 + 1$,

$$hc/\lambda = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}((n_1 + 1)^2 - n_1^2) = \left(\frac{\pi}{L}\right)^2 \frac{\hbar^2}{2m}(2n_1 + 1)$$

Molecules that have a longer conjugated system will absorb light of longer wavelengths (less energy), and molecules with a shorter conjugated system will absorb light of shorter wavelengths (higher energy). For example, consider the following molecule, which is a member of a family of fluorescent dyes known as cyanines. The conjugated system contains 8 π electrons, and the molecule absorbs light of around 550 nm. This wavelength corresponds to the green region of the visible spectrum. The solution absorbs green and lets everything else reach your eye. Red is the complementary color of green, so this molecule in solution will look red to you.



Now look at this other cyanine, which has two extra π electrons:



The particle in a box model tells you that this cyanine should absorb light of longer wavelengths (less energy), so it should not surprise you to know that a solution of this compound absorbs light of about 670 nm. This corresponds to the orange-red region of the spectrum, and the solution will look blue to us. If we instead shorten the conjugated chain we will produce a compound that absorbs in the blue (450 nm), and that will be yellow when in solution. We just connected differential equations, quantum mechanics and the colors of things... impressive!

5.5: Problems

Problem [Math Processing Error]

Solve the following initial value problems:

1. [Math Processing Error]
2. [Math Processing Error]
3. [Math Processing Error]
4. [Math Processing Error]

Problem [Math Processing Error]

The simple harmonic oscillator consists of a body moving in a straight line under the influence of a force whose magnitude is proportional to the displacement [Math Processing Error] of the body from the point of equilibrium, and whose direction is towards this point. [Math Processing Error] The force acts in the direction opposite to that of the displacement. The constant [Math Processing Error] is a measure of how hard or soft the spring is.

Newton's law of motion states that the force applied on an object equals its mass multiplied by its acceleration. The variable [Math Processing Error] represents the displacement of the spring from its undistorted length, and the acceleration is the second derivative of the displacement. Therefore: [Math Processing Error]

Combining equations [Math Processing Error] and [Math Processing Error] we obtain: [Math Processing Error]

which is a second order differential equation. Notice that [Math Processing Error] (the mass of the body) and [Math Processing Error] (the spring constant) are not functions of [Math Processing Error].

Assume that the displacement [Math Processing Error] and the velocity [Math Processing Error] at time [Math Processing Error] are: [Math Processing Error] and [Math Processing Error]. Physically, this means that the displacement at time zero is [Math Processing Error], and the body is at rest.

[Math Processing Error] Obtain an expression for [Math Processing Error].

[Math Processing Error] What is the period of the function you found above?

In the example above we assumed that the forces due to friction were negligible. If the oscillator moves in a viscous medium, we need to include a frictional term in Newton's equation. The force due to friction is proportional to the velocity of the mass ([Math Processing Error]), and the direction is opposite to the displacement. Therefore:

[Math Processing Error]

where [Math Processing Error] is a constant that depends on the viscosity of the medium.

[Math Processing Error] Obtain an expression for [Math Processing Error]. You will have to consider the cases [Math Processing Error], [Math Processing Error] and [Math Processing Error] separately. The answers are printed below so you can check your results. Be sure you show all your work step by step.

- [Math Processing Error]:

  [Math Processing Error]

- [Math Processing Error]:

  [Math Processing Error]

- [Math Processing Error]:

  [Math Processing Error]

? Problem [Math Processing Error]

Find the eigenfunctions ([Math Processing Error]) and eigenvalues [Math Processing Error] of the following boundary value problems:

- [Math Processing Error], [Math Processing Error]
- [Math Processing Error], [Math Processing Error]

CHAPTER OVERVIEW

6: Power Series Solutions of Differential Equations

Objectives

- Learn how to solve second order ODEs using series.
- Use the power series method to solve the Laguerre equation.

6.1: Introduction to Power Series Solutions of Differential Equations

In Chapter 5 we discussed a method to solve linear homogeneous second order differential equations with constant coefficients. Many important differential equations in physical chemistry are second order homogeneous linear differential equations, but do not have constant coefficients. The following examples are all important differential equations in the physical sciences:

- Hermite equation: *[Math Processing Error]*
- Laguerre equation: *[Math Processing Error]*
- Legendre equation: *[Math Processing Error]*

These equations do not have constant coefficients because some of the terms multiplying *[Math Processing Error]* and *[Math Processing Error]* are functions of *[Math Processing Error]*. In order to solve these differential equations, we will assume that the solution, *[Math Processing Error]*, can be expressed as a Maclaurin series:

[Math Processing Error]

This method will give us a series as the solution, but at this point we know that an infinite series is one way of representing a function, so we will not be too surprised. For example, instead of obtaining *[Math Processing Error]* as the solution, we will get the series *[Math Processing Error]*, which of course represents the same thing. Does it mean that we need to know all the series to be able to recognize which function is represented by the series we got as the answer? Not really. We will see that this method is useful when the solution can be expressed only as a series, but not as a known function. Even if this is the case, for simplicity we will see how the method works with a problem whose solution is a known function. We will then move to a problem whose solution can be expressed as a series only.

6.2: The Power Series Method

We will use the series method to solve

$$\frac{dy}{dx} + y = 0 \tag{6.2.1}$$

This equation is a first order separable differential equation, and can be solved by direct integration to give ce^{-x} (be sure you can do this on your own). In order to use the series method, we will first assume that the answer can be expressed as

$$y(x) = \sum_{n=0}^{\infty} a_n x^n.$$

Again, instead of obtaining the actual function $y(x)$, in this method we will obtain the series

$$\sum_{n=0}^{\infty} a_n x^n.$$

We will use the expression

$$y(x) = a_0 + a_1 x + a_2 x^2 \ldots a_n x^n \tag{6.2.2}$$

to calculate the derivatives we need and substitute in the differential equation. Given our initial assumption that the solution can be written as:

$$y(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots + a_n x^n$$

we can write the first derivative as:

$$y'(x) = a_1 + a_2 \times 2x + a_3 \times 3x^2 + \ldots + a_n \times n x^{n-1}$$

We'll substitute these expressions in the differential equation we want to solve (Equation 6.2.1):

$$\frac{dy}{dx} + y = 0$$

$$\left(a_1 + a_2 \times 2x + a_3 \times 3x^2 + \ldots + a_n \times n x^{n-1}\right) + \left(a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots + a_n x^n\right) = 0$$

and group the terms that have the same power of x:

$$(a_1 + a_0) + (2a_2 + a_1)x + (3a_3 + a_2)x^2 + (4a_4 + a_3)x^3 + \ldots = 0$$

This expression needs to hold for all values of x, so all terms in parenthesis need to be zero:

$$(a_1 + a_0) = (2a_2 + a_1) = (3a_3 + a_2) = (4a_4 + a_3) = \ldots = 0$$

The equations above give relationships among the different coefficients. Our solution will look like Equation 6.2.2, but we know now that these coefficients are all related to each other. In the next step, we will express all the coefficients in terms of a_0.

$$\begin{gathered}(a_1 + a_0) \rightarrow a_1 = -a_0 \\ (2a_2 + a_1) \rightarrow a_2 = -a_1/2 = a_0/2 \\ (3a_3 + a_2) \rightarrow a_3 = -a_2/3 = -a_0/6 \\ (4a_4 + a_3) \rightarrow a_4 = -a_3/4 = a_0/24\end{gathered}$$

We can continue, but hopefully you already see the pattern: $a_n = a_0 (-1)^n / n!$. We can then write our solution as:

$$y(x) = \sum_{n=0}^{\infty} a_n x^n = \sum_{n=0}^{\infty} a_0 \frac{(-1)^n}{n!} x^n = a_0 \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} x^n$$

We got our solution in the shape of an infinite series. Again, in general, we will be happy with the result as it is, because chances are the series does not represent any combination of known functions. In this case, however, we know that the solution is $y(x) = ce^{-x}$, so it should not surprise you that the series

$$\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}x^n$$

is the Maclaurin series of e^{-x}. The constant a_0 is an arbitrary constant, and can be calculated if we have an initial condition.

The same procedure can be performed more elegantly in the following way:

$$y(x)=\sum_{n=0}^{\infty}a_nx^n$$

$$y'(x)=\sum_{n=1}^{\infty}na_nx^{n-1}$$

$$y'(x)+y(x)\ =0\rightarrow\sum_{n=1}^{\infty}na_nx^{n-1}+\sum_{n=0}^{\infty}a_nx^n=0$$

changing the 'dummy' index of the first sum:

$$\sum_{n=0}^{\infty}(n+1)a_{n+1}x^n+\sum_{n=0}^{\infty}a_nx^n=0$$

and combining the two sums:

$$\sum_{n=0}^{\infty}\left[(n+1)a_{n+1}+a_n\right]x^n=0$$

Because this result needs to be true for all values of x:

$$(n+1)a_{n+1}+a_n=0\rightarrow\frac{a_{n+1}}{a_n}=-\frac{1}{n+1}$$

The expression above is what is known as a recursion formula. It gives the value of the second coefficient in terms of the first, the third in terms of the second, etc.

$$\frac{a_{n+1}}{a_n}=-\frac{1}{n+1}\rightarrow\frac{a_1}{a_0}=-1;\ \frac{a_2}{a_1}=-\frac{1}{2};\ \frac{a_3}{a_2}=-\frac{1}{3};\ \frac{a_4}{a_3}=-\frac{1}{4}\ldots$$

We know we want to express all the coefficients in terms of a_0. We can achieve this by multiplying all these terms:

$$\frac{a_1}{a_0}\frac{a_2}{a_1}\frac{a_3}{a_2}\ldots\frac{a_n}{a_{n-1}}\ldots=\frac{a_n}{a_0}$$

$$\frac{a_n}{a_0}=-1\times\left(-\frac{1}{2}\right)\times\left(-\frac{1}{3}\right)\times\left(-\frac{1}{4}\right)\ldots\times\left(-\frac{1}{n}\right)=\frac{(-1)^n}{n!}$$

and therefore, $a_n=a_0\dfrac{(-1)^n}{n!}$

Note: You do not need to worry about being 'elegant'. It is fine if you prefer to take the less 'elegant' route!

✓ Example 6.2.1

Solve the following equation using the power series method:

$$\frac{d^2y}{dx^2}+y=0$$

Solution

We start by assuming that the solution can be written as:

$$y(x)=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\ldots$$

and therefore the first and second derivatives are:

$$\begin{aligned} y'(x) &= a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4\dots \\ y''(x) &= 2a_2+2\times 3a_3x+3\times 4a_4x^2+4\times 5a_5x^3+5\times 6a_6x^4\dots \end{aligned}$$

Notice that up to this point, this procedure is independent of the differential equation we are trying to solve.

We now substitute these expressions in the differential equation:

$$(2a_2+2\times 3a_3x+3\times 4a_4x^2+4\times 5a_5x^3+5\times 6a_6x^4\dots)+(a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\dots)=0$$

and group the terms in the same power of x:

$$(2a_2+a_0)+(2\times 3a_3+a_1)x+(3\times 4a_4+a_2)x^2+(4\times 5a_5+a_3)x^3+(5\times 6a_6+a_4)x^4\dots=0$$

Because this needs to be true for all values of x, all the terms in parenthesis need to equal zero.

$$(2a_2+a_0)=(2\times 3a_3+a_1)=(3\times 4a_4+a_2)=(4\times 5a_5+a_3)=(5\times 6a_6+a_4)\dots=0$$

We have relationships between the odd coefficients and between the even coefficients, but we see that the odd and the even are not related. Let's write all the odd coefficients in terms of a_1, and the even coefficients in terms of a_0:

$a_2=-\frac{a_0}{2}=-\frac{a_0}{2!}$	$a_3=-\frac{a_1}{(2\times 3)}=-\frac{a_1}{3!}$
$a_4=-\frac{a_2}{(3\times 4)}=\frac{a_0}{(2\times 3\times 4)}=\frac{a_0}{4!}$	$a_5=-\frac{a_3}{(4\times 5)}=\frac{a_1}{(2\times 3\times 4\times 5)}=\frac{a_1}{5!}$
$a_6=-\frac{a_4}{(5\times 6)}=-\frac{a_0}{(2\times 3\times 4\times 5\times 6)}=-\frac{a_0}{6!}$	$a_7=-\frac{a_5}{(6\times 7)}=-\frac{a_1}{(2\times 3\times 4\times 5\times 6\times 7)}=-\frac{a_1}{7!}$

Substituting these relationships in the expression of $y(x)$:

$$\begin{aligned} y(x) &= a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\dots && (6.2.3)\\ &= a_0+a_1x-\frac{a_0}{2!}x^2-\frac{a_1}{3!}x^3+\frac{a_0}{4!}x^4+\frac{a_1}{5!}x^5-\frac{a_0}{6!}x^6-\frac{a_1}{7!}x^7+\dots && (6.2.4)\\ &= a_0(1-\frac{1}{2!}x^2+\frac{1}{4!}x^4-\frac{1}{6!}x^6\dots)+a_1(x-\frac{1}{3!}x^3+\frac{1}{5!}x^5-\frac{1}{7!}x^7+\dots) && (6.2.5) \end{aligned}$$

which can be expressed as:

$$y(x)=a_0\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n)!}x^{2n}+a_1\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)!}x^{2n+1}$$

This is the solution of our differential equation.

If you check Chapter 3, you will recognize that these sums are the Maclaurin expansions of the functions cosine and sine. This should not surprise you, as the differential equation we just solved can be solved with the techniques we learned in Chapter 5 to obtain:

$$y(x)=c_1\cos x+c_2\sin x$$

Again,we used this example to illustrate the method, but it does not make a lot of sense to use the power series method to solve a ODE that can be solved using easier techniques. This method will be useful when the solution of the ODE can be only expressed as a power series.

6.3: The Laguerre Equation

So far we used the power series method to solve equations that can be solved using simpler methods. Let’s now turn our attention to differential equations that cannot be solved otherwise. One such example is the *Laguerre equation*. This differential equation is important in quantum mechanics because it is one of several equations that appear in the quantum mechanical description of the hydrogen atom. The solutions of the Laguerre equation are called the *Laguerre polynomials*, and together with the solutions of other differential equations, form the functions that describe the orbitals of the hydrogen atom.

The Laguerre equation is

$$xy''+(1-x)y'+ny=0$$

where $n=0,1,2....$

Solving the n=0 Laguerre Equation

Here, for simplicity, we will solve the equation for a given value of n. That is, instead of solving the equation for a generic value of n, we will solve it first for $n=0$, then for $n=1$, and so on.

Let’s start with $n=0$. The differential equation then becomes:

$$xy''+y'-xy'=0. \tag{6.3.1}$$

We start by assuming that the solution can be written as:

$$y(x)=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4+\ldots$$

and therefore the first and second derivatives are:

$$\begin{aligned} y'(x) &= a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4\ldots \\ y''(x) &= 2a_2+2\times 3a_3x+3\times 4a_4x^2+4\times 5a_5x^3+5\times 6a_6x^4+\ldots. \end{aligned}$$

We then plug these expressions in the differential equation (Equation 6.3.1):

$$\begin{aligned} xy''+y'-xy' &= 0 \\ x(2a_2+2\times 3a_3x+3\times 4a_4x^2+4\times 5a_5x^3+5\times 6a_6x^4+\ldots)+(a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4\ldots) \\ -x(a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4+\ldots) &= 0 \\ (2a_2x+2\times 3a_3x^2+3\times 4a_4x^3+4\times 5a_5x^4+5\times 6a_6x^5+\ldots)+(a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4+\ldots) \\ -(a_1x+2a_2x^2+3a_3x^3+4a_4x^4+5a_5x^5+\ldots) &= 0 \end{aligned}$$

We then group the terms in the same power of x. However, to avoid writing a long equation, let’s try putting the information in a table. The second column contains the terms that multiply each power of x. We know each of these terms needs to be zero, and that will give us the relationships between the coefficients we need.

x^0	a_1	$=0$	$\rightarrow a_1=0$
x^1	$2a_2+2a_2-a_1$	$=0$	$\rightarrow a_2=a_1/4$
x^2	$6a_3+3a_3-2a_2$	$=0$	$\rightarrow a_3=a_2\times 2/9$
x^3	$12a_4+4a_4-3a_3$	$=0$	$\rightarrow a_4=a_3\times 3/16$
x^4	$20a_5+5a_5-4a_4$	$=0$	$\rightarrow a_5=a_4\times 4/25$

The first row tells us that $a_1=0$, and from the other rows, we conclude that all other coefficients with $n>1$ are also zero. Recall that $y(x)=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\ldots$, so the solution is simply $y(x)=a_0$ (i.e. the solution is a constant). This solution may be disappointing to you because it is not a function of x. Don’t worry, we’ll get something more interesting in the next example.

Solving the n=1 Laguerre Equation

Let’s see what happens when $n=1$. The differential equation becomes

$$xy''+y'-xy'+y=0. \tag{6.3.2}$$

As always, we start by assuming that the solution can be written as:

$$y(x)=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4+\dots$$

and therefore the first and second derivatives are:

$$\begin{aligned} y'(x) &= a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4+\dots && (6.3.3)\\ y''(x) &= 2a_2+2\times 3a_3x+3\times 4a_4x^2+4\times 5a_5x^3+5\times 6a_6x^4+\dots && (6.3.4)\end{aligned}$$

and then plug these expressions in the differential equation (Equation 6.3.2):

$$\begin{aligned} xy''+y'-xy'+y &= 0\\ x(2a_2+2\times 3a_3x+3\times 4a_4x^2+4\times 5a_5x^3+5\times 6a_6x^4\dots)+(a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4\dots) &= 0\\ -x(a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4\dots)+(a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\dots)\\ (2a_2x+2\times 3a_3x^2+3\times 4a_4x^3+4\times 5a_5x^4+5\times 6a_6x^5\dots)+(a_1+2a_2x+3a_3x^2+4a_4x^3+5a_5x^4\dots) &= 0\\ -(a_1x+2a_2x^2+3a_3x^3+4a_4x^4+5a_5x^5\dots)+(a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\dots)\end{aligned}$$

The next step is to group the terms in the same power of x. Let’s make a table as we did before:

x^0	a_1+a_0	$=0$	$\rightarrow a_1=-a_0$
x^1	$2a_2+2a_2-a_1+a_1$	$=0$	$\rightarrow 4a_2=0$
x^2	$6a_3+3a_3-2a_2+a_2$	$=0$	$\rightarrow a_3=a_2\times 1/9$
x^3	$12a_4+4a_4-3a_3+a_3$	$=0$	$\rightarrow a_4=a_3\times 2/16$
x^4	$20a_5+5a_5-4a_4+a_4$	$=0$	$\rightarrow a_5=a_4\times 3/25$

We see that in this case $a_1=-a_0$, and $a_{n>1}=0$. Recall that

$$y(x)=a_0+a_1x+a_2x^2+a_3x^3+a_4x^4\dots$$

so the solution is $y(x)=a_0(1-x)$.

In physical chemistry, we define the Laguerre polynomials ($L_n(x)$) as the solution of the Laguerre equation with $a_0=n!$. This is arbitrary and somewhat field-dependent. You may find other definitions, but we’ll stick with $n!$ because it is the one that is more widely used in physical chemistry.

With the last two examples we proved that $L_0(x)=1$ and $L_1(x)=1-x$. You’ll obtain $L_2(x)$ and $L_3(x)$ in your homework.

6.4: Problems

Problem 6.4.1

Solve the following differential equation

$$(1-x)y'(x)-y=0$$

using 1) the separation of variables method and 2) the power series method, and prove that the two solutions are mathematically equivalent.

Problem 6.4.2

Solve the following differential equation

$$y''(x)-y(x)=0$$

using 1) the method we have learned for second order ODEs with constant coefficients and 2) the power series method, and prove that the two solutions are mathematically equivalent.

Problem 6.4.1

Solve the Laguerre equation with $n=2$ and $n=3$. Write down $L_2(x)$ and $L_3(x)$

CHAPTER OVERVIEW

7: Fourier Series

Chapter Objectives

- Learn how to express periodic functions, identify them as even, odd or neither, and calculate their period.
- Compute the Fourier series of periodic functions.
- Understand the concept of orthogonal expansions and orthonormal functions.

7.1: Introduction to Fourier Series

In Chapter 3 we learned that a function $f(x)$ can be expressed as a series in powers of x as long as $f(x)$ and all its derivatives are finite at $x = 0$. We then extended this idea to powers of $x - h$, and called these series “Taylor series”. If $h = 0$, the functions that form the basis set are the powers of $x : x^0, x^1, x^2 \ldots$, and in the more general case of $h \neq 0$, the basis functions are $(x-h)^0, (x-h)^1, (x-h)^2 \ldots$

The powers of x or $(x - h)$ are not the only choice of basis functions to expand a function in terms of a series. In fact, if we want to produce a series which will converge rapidly, so that we can truncate if after only a few terms, it is a good idea to choose basis functions that have as much as possible in common with the function to be represented. If we want to represent a periodic function, it is useful to use a basis set containing functions that are periodic themselves. For example, consider the following set of functions: $\sin(nx),\ n = 1, 2, \ldots, \infty$:

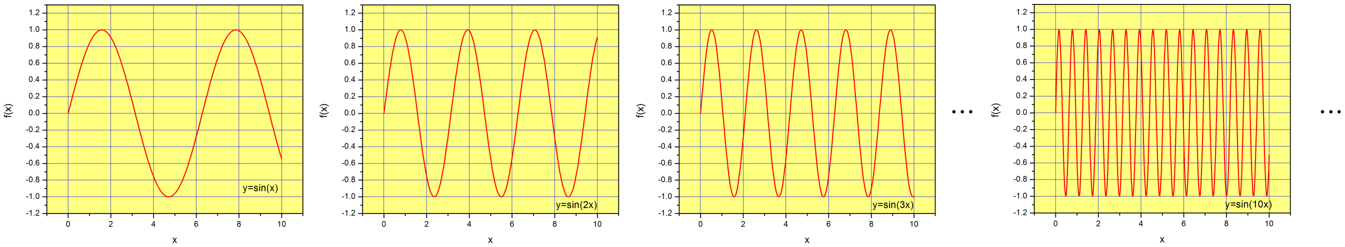


Figure 7.1.1: Some examples of the family of funtions $\sin(nx)$. From left to right: $\sin(x), \sin(2x), \sin(3x)$ and $\sin(10x)$ (CC BY-NC-SA; Marcia Levitus)

We can mix a finite number of these functions to produce a periodic function like the one shown in the left panel of Figure 7.1.2, or an infinite number of functions to produce a periodic function like the one shown on the right. Notice that an infinite number of sine functions creates a function with straight lines! We will see that we can create all kinds of periodic functions by just changing the coefficients (i.e. the numbers multiplying each sine function).

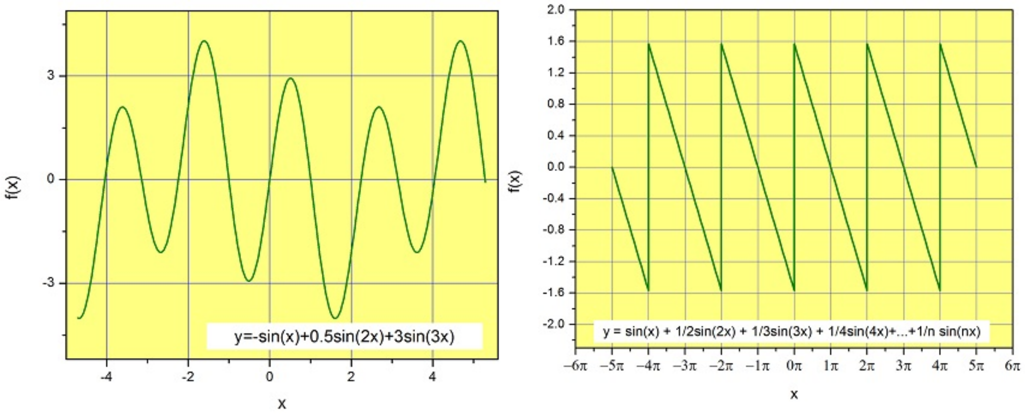


Figure 7.1.2: Examples of periodic functions that are linear combinations of $sin(nx)$ (CC BY-NC-SA; Marcia Levitus)

So far everything sounds fine, but we have a problem. The functions $\sin nx$ are all odd, and therefore any linear combination will produce an odd periodic function. We might need to represent an even function, or a function that is neither odd nor even. This tells us that we need to expand our basis set to include even functions, and I hope you will agree the obvious choice are the cosine functions $\cos(nx)$.

Below are two examples of even periodic functions that are produced by mixing a finite (left) or infinite (right) number of cosine functions. Notice that both are even functions.

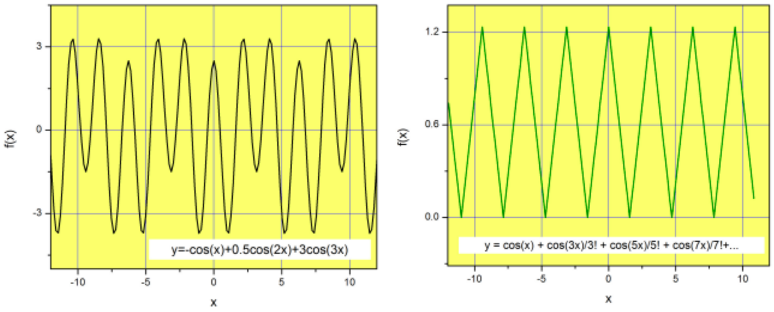


Figure $7.1.3$: Examples of periodic functions that are linear combinations of $\cos(nx)$ functions (CC BY-NC-SA; Marcia Levitus)

Before moving on, we need to review a few concepts. First, since we will be dealing with periodic functions, we need to define the period of a function. As we saw in Section 1.4, a function $f(x)$ is said to be periodic with period P if $f(x) = f(x + P)$. For example, the period of the function of Figure $7.1.4$ is 2π.

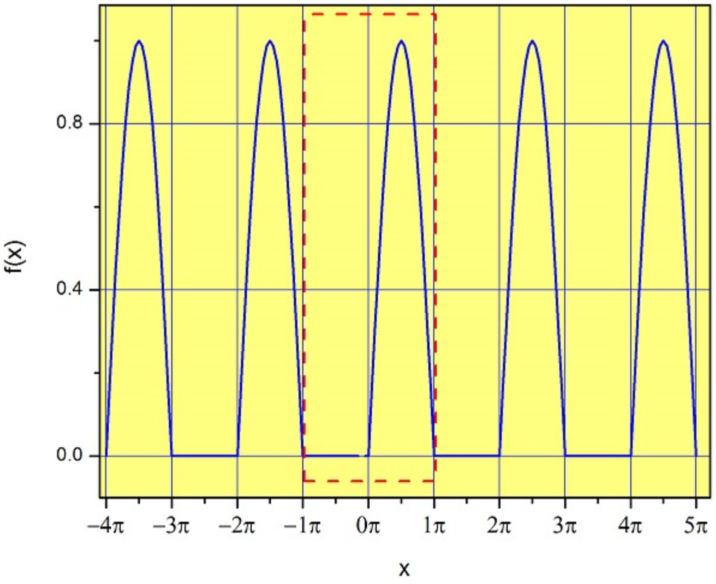


Figure $7.1.4$: A periodic function with period $P = 2\pi$ (CC BY-NC-SA; Marcia Levitus)

How do we write the equation for this periodic function? We just need to specify the equation of the function between $-P/2$ and $P/2$. This range is shown in a red dotted line in Figure $7.1.4$, and as you can see, it has the width of a period, and it is centered around $x = 0$. If we have this information, we just need to extend the function to the left and to the right to create the periodic function:

$$f(x)=\begin{cases}\sin x & 0\le x\le\pi\\ 0 & -\pi\le x\le 0\end{cases}$$

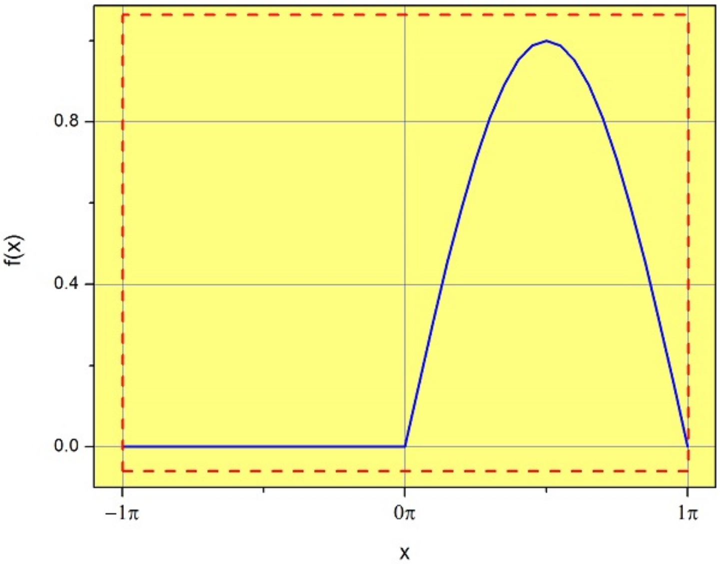


Figure 7.1.4 (CC BY-NC-SA; Marcia Levitus)

7.2: Fourier Series

A Fourier series is a linear combination of sine and cosine functions, and it is designed to represent periodic functions:

$$f(x)=\frac{a_0}{2}+\sum_{n=1}^{\infty}a_n\cos\left(\frac{n\pi x}{L}\right)+\sum_{n=1}^{\infty}b_n\sin\left(\frac{n\pi x}{L}\right) \tag{7.2.1}$$

The coefficients $a_0, a_1, a_2 \ldots a_n$ and $b_1, b_2 \ldots . b_n$ are constants.

It is important to notice that the period of the sine and cosine functions in Equation 7.2.1 is $P=2L/n$ (see Section 1.4). This means that we will be mixing sines and cosines of periods $2L$, $2L/2$, $2L/3$, $2L/4$, etc. As we will see, this linear combination will result in a periodic function of period $P=2L$.

In addition, we need only the odd terms (the sine functions) to represent an odd periodic function, so in this case all the a_n coefficients (including a_0) will be zero. We need only even terms (the cosine functions) to represent an even function, so in this case all the b_n coefficients will be zero. Why don't we have a b_0 term? This is because $\sin(0)=0$. In the case of the cosine terms, the $n=0$ term is separated from the sum, but it does not vanish because $\cos(0)\neq 0$.

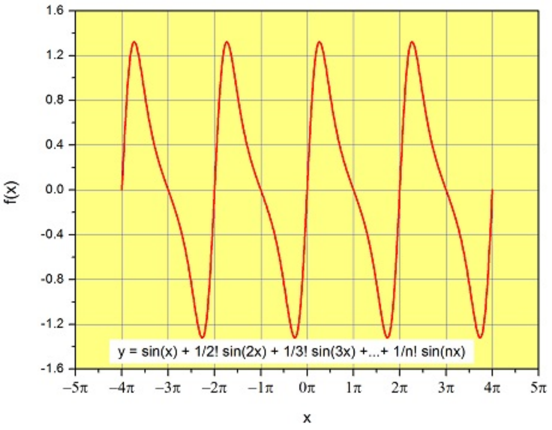
This means that an odd periodic function with period $P=2L$ will be in general:

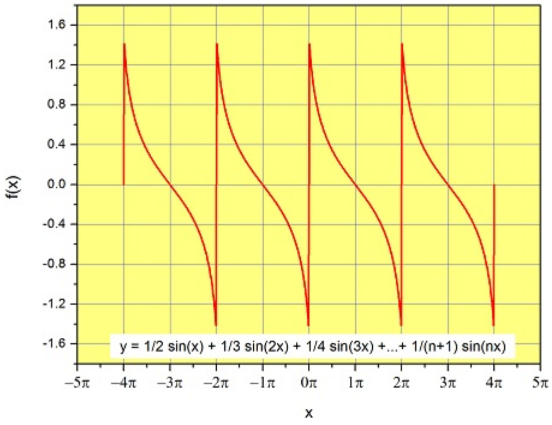
$$f(x)=b_1\sin\left(\frac{\pi x}{L}\right)+b_2\sin\left(\frac{2\pi x}{L}\right)+b_3\sin\left(\frac{3\pi x}{L}\right)\ldots$$

Let's say we want to construct an odd periodic function of period $P=2\pi$. Because the period is $2L$, this means that $L=\pi$:

$$f(x)=b_1\sin(x)+b_2\sin(2x)+b_3\sin(3x)\ldots$$

We in fact already saw an example like this in Figure $7.1.2$ (right). This periodic function, which is constructed using $b_n=1/n$, has a period of 2π as we just predicted. Let's see other examples with different coefficients:





Notice that we are mixing the functions $\sin(x), \sin(2x), \sin(3x)\ldots$ using different coefficients, and always create a periodic function with period $P=2\pi$.

Coming back to Equation 7.2.1, we know that different coefficients will create different periodic functions, but they will all have a period $2L$. The obvious question now is how to calculate the coefficients that will create the function we want. Let's say that the periodic function is constructed by a periodic extension of the function $f(x)$, which is defined in the interval $[-L,L]$. One example would be the function of Figure $7.1.5$, which is defined in the interval $[-\pi,\pi]$. If we create the periodic extension of this function, we will create a periodic function with period 2π. Analogously, by creating a periodic extension of a function defined in the interval $[-L,L]$ we will create a periodic function with period $2L$. The coefficients of Equation 7.2.1 are calculated as follows:

$$a_0=\frac{1}{L}\int_{-L}^{L}f(x)dx \tag{7.2.2}$$

$$a_n=\frac{1}{L}\int_{-L}^{L}f(x)\cos\left(\frac{n\pi x}{L}\right)dx \tag{7.2.3}$$

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)dx \tag{7.2.4}$$

Notice that Equation 7.2.2 is a special case of Equation 7.2.3, and that we don't have a coefficient b_0 because $\sin(0) = 0$. Because Equation 7.2.1 represents a periodic function with period $2L$, the integration is performed over one period centered at zero (that is, L is half the period).

Alternative Formulation

Equation 7.2.1 is often written as:

$$f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right) \tag{7.2.5}$$

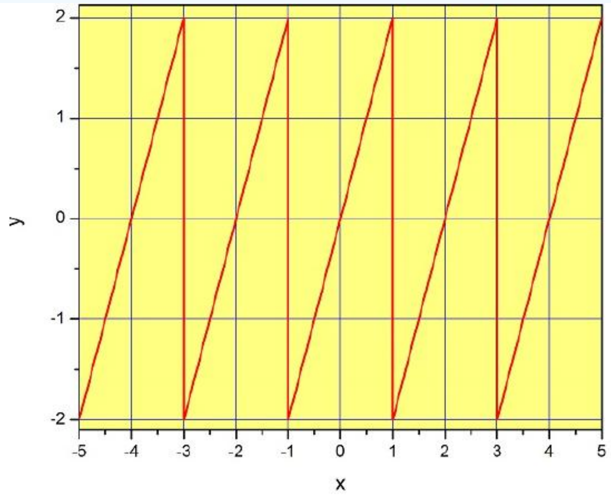
If we choose to do this, we of course need to re-define the coefficient a_0 as:

$$a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)dx.$$

Both versions give of course the same series, and whether you choose one or the other is a matter of taste. You may see the two versions in different textbooks, so don't get confused!.

✓ Example 7.2.1

Obtain the Fourier series of the periodic function represented in the figure.



Solution

$y(x)$ is a periodic function with period $P = 2$. It can be constructed by the periodic extension of the function $f(x) = 2x$, defined in the interval $[-1, 1]$. Notice that this interval has a width equal to the period, and it is centered at zero.

Because $y(x)$ is odd, we will not bother calculating the coefficients a_n. We could, but we would obtain zero for all of them. Equation 7.2.1, therefore, reduces to:

$$y(x) = \sum_{n=1}^{\infty} b_n sin\left(\frac{n\pi x}{L}\right)$$

From Equation 7.2.4, the coefficients b_n are calculated as:

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)dx$$

and in this case, because $L = 1$ (half the period),

$$b_n = \int_{-1}^{1} (2x)\sin(n\pi x)dx = 2\int_{-1}^{1} x\sin(n\pi x)dx$$

The primitive of $\int x\sin(ax)dx$ is $\dfrac{\sin(ax)}{a^2} - \dfrac{x\cos(ax)}{a}$ (see formula sheet), so

$$b_n = 2\int_{-1}^{1} x\sin(n\pi x)dx = 2\left[\frac{\sin(n\pi)}{(n\pi)^2} - \frac{\cos(n\pi)}{n\pi} - \left(\frac{\sin(n\pi(-1))}{(n\pi)^2} - \frac{(-1)\cos(n\pi(-1))}{n\pi}\right)\right]$$

Using the fact that $\sin(n\pi)$ is zero and $\cos x$ is an even function:

$$b_n = -4\frac{\cos(n\pi)}{n\pi}$$

Let's write a few terms in a table:

n	$\cos(n\pi)$	b_n
1	-1	$\frac{4}{\pi}$
2	1	$-\frac{4}{2\pi}$
3	-1	$\frac{4}{3\pi}$
4	1	$-\frac{4}{4\pi}$
5	-1	$\frac{4}{5\pi}$

A general expression for b_n is:

$$b_n = 4\frac{(-1)^{n+1}}{n\pi}$$

The series

$$y(x) = \sum_{n=1}^{\infty} b_n sin\left(\frac{n\pi x}{L}\right)$$

is then:

$$y(x) = \frac{4}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n} sin(n\pi x) \tag{7.2.6}$$

As in the case of a Taylor series, Equation 7.2.6 is exact if we include the infinite terms of the series. If we truncate the series using a finite number of terms, we will create an approximation. Figure 7.2.1 shows an example with 1, 2, 3 and 8 terms.

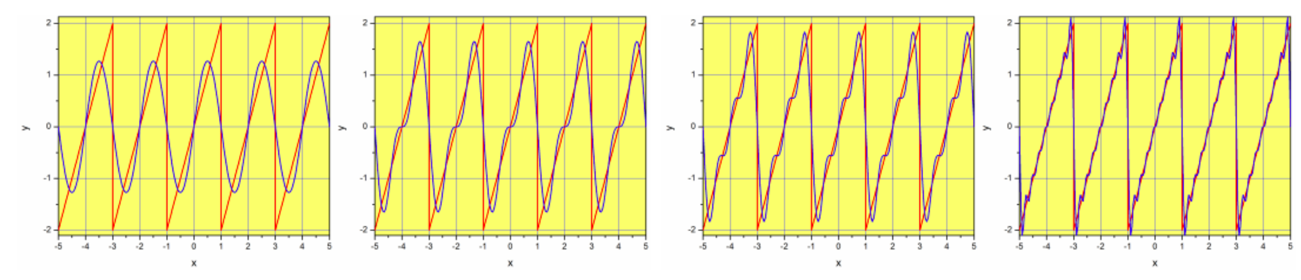


Figure 7.2.1: The sawtooth periodic function of Example 7.1 superimposed to the functions \frac{4}{\pi} \sum_{n=1}^m \frac{(-1)^{n+1}}{n} \sin (n \pi x)\) with $m = 1,\ 2,\ 3$ and 8. (CC BY-NC-SA; Marcia Levitus)

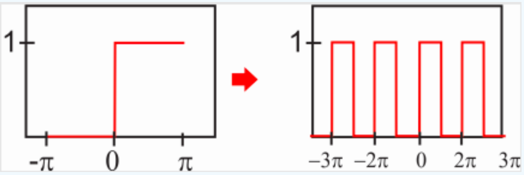
Example 7.2.2

Obtain the Fourier series of the square wave formed by the periodic extension of the function:

$$f(x)=\begin{cases}0 & -\pi\leq x\leq 0\\ 1 & 0<x\leq\pi\end{cases}$$

Solution

The periodic extension of the function $f(x)$ produces a periodic function with period 2π:



Strictly speaking, the resulting periodic function is neither even nor odd, so we would need to calculate all the coefficients. However, you may notice that the function would be odd if we were to subtract 1/2 from all points. In other words, the periodic function we are looking for will be a constant (a_0) plus an odd periodic function (sine series). We will calculate the constant, but from this discussion it should be obvious that we will get $a_0/2=1/2$. We will also calculate the rest of the a_n coefficients, but we now know they will all be zero.

The first coefficient, a_0 is (Equation 7.2.2):

$$a_0=\frac{1}{L}\int_{-L}^{L}f(x)dx$$

Here, $L=\pi$ (half the period), so:

$$a_0=\frac{1}{\pi}\int_{-\pi}^{\pi}f(x)dx=\frac{1}{\pi}\int_{0}^{\pi}1dx=1$$

where we have used the fact that $f(x)=0$ in the interval $-\pi<x<0$. The coefficients a_n are (Equation 7.2.3)

$$a_n=\frac{1}{L}\int_{-L}^{L}f(x)\cos\left(\frac{n\pi x}{L}\right)dx=\frac{1}{\pi}\int_{0}^{\pi}\cos(nx)dx=\frac{1}{\pi}\left(\frac{sin(n\pi))}{n}\right)\Big|_0^\pi=0$$

The coefficients b_n are (Equation 7.2.4)

$$b_n=\frac{1}{L}\int_{-L}^{L}f(x)\sin\left(\frac{n\pi x}{L}\right)dx=\frac{1}{\pi}\int_{0}^{\pi}\sin(nx)dx=\frac{1}{\pi}\left(-\frac{cos(n\pi))}{n}\right)\Big|_0^\pi=-\frac{1}{\pi n}(\cos(n\pi)-cos(0))$$
$$=\frac{1-\cos(n\pi)}{n\pi}$$

Let’s see a few terms in a table:

n	1	2	3	4	5	6
$\cos(n\pi)$	-1	1	-1	1	-1	1
b_n	$\frac{2}{\pi}$	0	$\frac{2}{3\pi}$	0	$\frac{2}{5\pi}$	0

The series is (Equation 7.2.1)

$$f(x)=\frac{a_0}{2}+\sum_{n=1}^{\infty}a_n cos\left(\frac{n\pi x}{L}\right)+\sum_{n=1}^{\infty}b_n sin\left(\frac{n\pi x}{L}\right)$$

and with the coefficients we got we can write:

$$f(x)=\frac{1}{2}+\frac{2}{\pi}\sin(x)+\frac{2}{3\pi}\sin(3x)+\frac{2}{5\pi}\sin(5x)\ldots$$

or more elegantly:

$$\frac{1}{2}+\frac{2}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin[(2n+1)x]$$

Notice that, as expected, we have a sine series (which represents and odd periodic function) plus a constant (which ’pushes’ the function up).

Need help? The links below contain solved examples.

External links:

- Fourier series example I: http://www.youtube.com/watch?v=jzzpxqVohhI
- Fourier series example II: http://www.youtube.com/watch?v=edwG9x5v3Xo

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7.3: Orthogonal Expansions

Note

As stated in Section 7.2, the coefficients of 7.3.7 are defined as so:

$$a_0 = \frac{1}{L}\int_{-L}^{L} f(x)dx \tag{7.3.1}$$

$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)dx \tag{7.3.2}$$

$$b_n = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{n\pi x}{L}\right)dx \tag{7.3.3}$$

The idea of expressing functions as a linear combination of the functions of a given basis set is more general than what we just saw. The sines and cosines are not the only functions we can use, although they are a particular good choice for periodic functions. There is a fundamental theorem in function theory that states that we can construct any function using a **complete set** of orthonormal functions.

The term orthonormal means that each function in the set is normalized, and that all functions of the set are mutually orthogonal. For a function in one dimension, the normalization condition is:

$$\int_{-\infty}^{\infty} |f(x)|^2 \, dx = 1 \tag{7.3.4}$$

Two functions $f(x)$ and $g(x)$ are said to be orthogonal if:

$$\int_{-\infty}^{\infty} f(x)g^*(x) \, dx = 0 \tag{7.3.5}$$

The idea that you can construct a function with a linear combination of orthonormal functions is analogous to the idea of constructing a vector in three dimensions by combining the vectors $\vec{v_1} = \{(1,0,0)\}, \vec{v_2} = \{(0,1,0)\}, \vec{v_3} = \{(0,0,1)\}$, which as we all know are mutually orthogonal, and have unit length.

The basis set we use to construct a Fourier series is

$$\{1, \sin\left(\frac{\pi}{L}x\right), \cos\left(\frac{\pi}{L}x\right), \sin\left(2\frac{\pi}{L}x\right), \cos\left(2\frac{\pi}{L}x\right), \sin\left(3\frac{\pi}{L}x\right), \cos\left(3\frac{\pi}{L}x\right)\ldots\}$$

We will prove that these functions are mutually orthogonal in the interval $[0, 2L]$ (one period).

For example, let's prove that $\sin\left(n\frac{\pi}{L}x\right)$ and 1 are orthogonal:

$$\int sin\left(\frac{n\pi x}{L}\right) dx = -\frac{L}{n\pi} cos\left(\frac{n\pi x}{L}\right)$$

$$\int_0^{2L} sin\left(\frac{n\pi x}{L}\right) dx = -\frac{L}{n\pi} cos\left(2n\pi\right) + \frac{L}{n\pi} cos(0) = \frac{L}{n\pi}(1 - cos(2n\pi)) = 0$$

We can also prove that any $\sin(nx)$ is orthogonal to any $\cos(nx)$:

$$\int sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi x}{L}\right)dx = -\frac{L}{4n\pi}\cos\left(\frac{2n\pi x}{L}\right)$$

$$\int_0^{2L} \sin\left(\frac{n\pi x}{L}\right) cos\left(\frac{n\pi x}{L}\right) dx = -\frac{L}{4n\pi}\cos(4n\pi) + \frac{L}{4n\pi}\cos(0) = 0$$

Following the same procedure, we can also prove that

$$\int \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{m\pi x}{L}\right)dx = 0 \;\; n \neq m$$

$$\int \cos\left(\frac{n\pi x}{L}\right)\cos\left(\frac{m\pi x}{L}\right)dx = 0 \; n \neq m$$

The functions used in a Fourier series are mutually orthogonal. Are they normalized?

$$\int_0^{2L} \sin^2\left(\frac{n\pi x}{L}\right)dx = L$$

$$\int_0^{2L} \cos^2\left(\frac{n\pi x}{L}\right)dx = L$$

$$\int_0^{2L} 1^2 \; dx = 2L$$

They are not! The functions $1/2L$, $\frac{1}{L}\sin\left(\frac{\pi}{L}x\right)$ and $\frac{1}{L}\cos\left(\frac{\pi}{L}x\right)$ are normalized, so we may argue that our orthonormal set should be:

$$\{\frac{1}{2L}, \frac{1}{L}\sin\left(\frac{\pi}{L}x\right), \frac{1}{L}\cos\left(\frac{\pi}{L}x\right), \frac{1}{L}\sin\left(2\frac{\pi}{L}x\right), \frac{1}{L}\cos\left(2\frac{\pi}{L}x\right), \ldots\}$$

and the series should be written as:

$$f(x) = c_0\frac{1}{2L} + \frac{1}{L}\sum_{n=1}^{\infty} c_n\cos\left(\frac{n\pi x}{L}\right) + \frac{1}{L}\sum_{n=1}^{\infty} d_n\sin\left(\frac{n\pi x}{L}\right) \tag{7.3.6}$$

where we used the letters c and d to distinguish these coefficients from the ones defined in Equations 7.3.1, 7.3.2 and 7.3.3.

However if we compare this expression to Equation 7.3.7:

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n sin\left(\frac{n\pi x}{L}\right) \tag{7.3.7}$$

we see that it is just a matter of how we define the coefficients. The coefficients in Equation 7.3.7 equal the coefficients in Equation 7.3.6 divided by L. In other words, the coefficients in Equation 7.3.7 already contain the constant L (look at Equations 7.3.1, 7.3.2 and 7.3.3), so we can write the sines and cosines without writing the factor $1/L$ every single time.

In conclusion, the set

$$\{1, \sin\left(\frac{\pi}{L}x\right), \cos\left(\frac{\pi}{L}x\right), \sin\left(2\frac{\pi}{L}x\right), \cos\left(2\frac{\pi}{L}x\right), \sin\left(3\frac{\pi}{L}x\right), \cos\left(3\frac{\pi}{L}x\right)\ldots\}$$

is not strictly orthonormal the way it is written, but it is once we include the constant L in the coefficients. Therefore, the cosines and sines form a complete set that allows us to express any other function using a linear combination of its members.

There are other orthonormal sets that are used in quantum mechanics to express a variety of functions. Just remember that we can construct any function using a complete set of orthonormal functions.

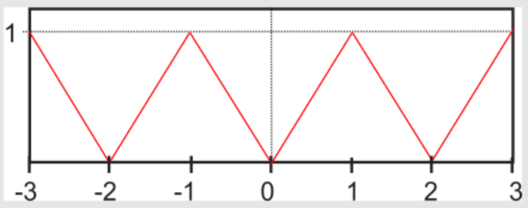
> *We can construct any function using a complete set of orthonormal functions.*

7.4: Problems

Note: You will use some of these results in Chapter 12. Keep a copy of your work handy so you can use it again when needed.

Problem 7.4.1

Consider the following periodic function:



- Is the function odd, even or neither?
- Calculate all the coefficients of the Fourier series of the function by hand (i.e. not in *Mathematica*). Express the function as a Fourier series.
- In the lab: Use the Manipulate function in *Mathematica* to plot the Fourier series. Observe how the finite sum gets closer to the actual triangular wave as you increase the upper bound of the sum.

Problem 7.4.2

Consider the periodic function formed by the periodic extension of:

$$f(x) = \begin{cases} -1/2 & -1 \leq x \leq 0 \\ 1/2 & 0 < x \leq 1 \end{cases}$$

- Is the function odd, even or neither?
- Calculate all the coefficients of the Fourier series of the function by hand (i.e. not in *Mathematica*). Express the function as a Fourier series.
- In the lab: Use the Manipulate function in *Mathematica* to plot the Fourier series.

Observe how the finite sum gets closer to the actual triangular wave as you increase the upper bound of the sum.

Problem 7.4.3

The following functions are encountered in quantum mechanics:

$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi},\ m = 0, \pm1, \pm2, \pm3 \ldots\ and\ 0 \leq \phi \leq 2\pi$

Prove that these functions are all normalized, and that any two functions of the set are mutually orthogonal.

Hint: Consider the cases $m = 0$ and $m \neq 0$ separately, and remember that $e^{im\phi} = 1$ when $m = 0$. Don't forget to take into account the complex conjugate in the normalization condition!

Hint 2: Check Chapter 2. You may have already solved this problem before!

CHAPTER OVERVIEW

8: Calculus in More than One Variable

Chapter Objectives

- Review the concept of partial derivative.
- Review the properties of partial derivatives.
- Be able to use the properties of partial derivatives in the context of physical chemistry problems.
- Review the concept of double and triple integrals.
- Learn the concept of equation of state. Understand the concept of a van der Waals gas from the molecular point of view.
- Learn about phase transitions and critical phenomena.

8.1: Functions of Two Independent Variables

A (real) function of one variable, $y = f(x)$, defines a curve in the plane. The first derivative of a function of one variable can be interpreted graphically as the slope of a tangent line, and dynamically as the rate of change of the function with respect to the variable Figure $8.1.1$.

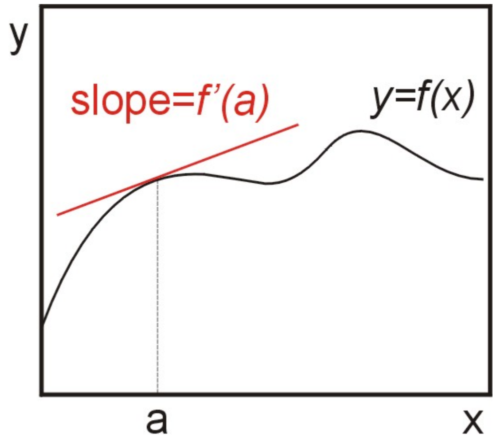


Figure $8.1.1$: Geometric interpretation of a derivative. (CC BY-NC-SA; Marcia Levitus)

A function of two independent variables, $z = f(x, y)$, defines a surface in three-dimensional space. For a function of two or more variables, there are as many independent first derivatives as there are independent variables. For example, we can differentiate the function $z = f(x, y)$ with respect to x keeping y constant. This derivative represents the slope of the tangent line shown in Figure $8.1.2$A. We can also take the derivative with respect to y keeping x constant, as shown in Figure $8.1.2$B.

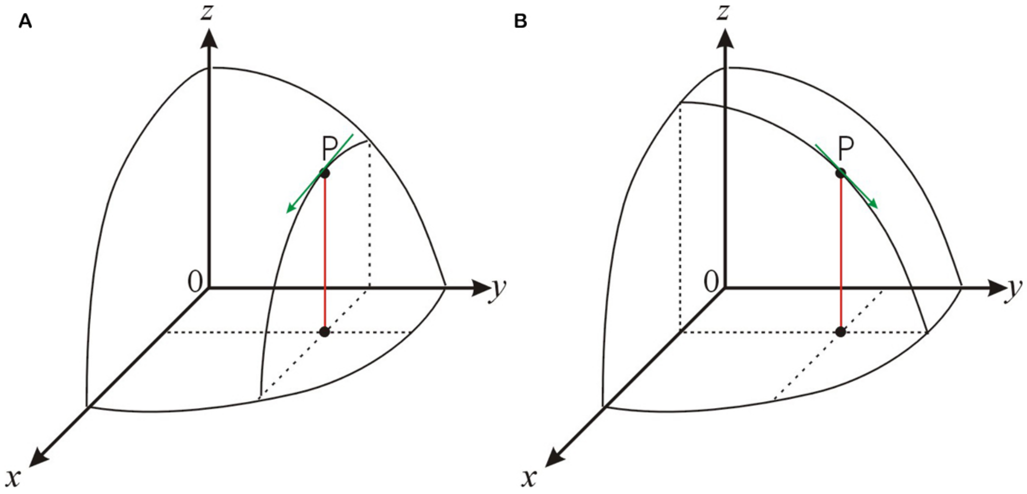


Figure $8.1.2$: Geometric interpretation of a partial derivative. (CC BY-NC-SA; Marcia Levitus)

For example, let's consider the function $z = 3x^2 - y^2 + 2xy$. We can take the derivative of this function with respect to x treating y as a constant. The result is $6x + 2y$. This is the partial derivative of the function with respect to x, and it is written:

$$\left(\frac{\partial z}{\partial x}\right)_y = 6x + 2y$$

where the small subscripts indicate which variables are held constant. Analogously, the partial derivate of z with respect to y is:

$$\left(\frac{\partial z}{\partial y}\right)_x = 2x - 2y$$

We can extend these ideas to functions of more than two variables. For example, consider the function $f(x, y, z) = x^2y/z$. We can differentiate the function with respect to x keeping y and z constant to obtain:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = 2x\frac{y}{z}$$

We can also differentiate the function with respect to z keeping x and y constant:

$$\left(\frac{\partial f}{\partial z}\right)_{x,y} = -x^2y/z^2$$

and differentiate the function with respect to y keeping x and z constant:

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} = \frac{x^2}{z}$$

Functions of two or more variables can be differentiated partially more than once with respect to either variable while holding the other constant to yield second and higher derivatives. For example, the function $z = 3x^2 - y^2 + 2xy$ can be differentiated with respect to x two times to obtain:

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x}\right)_y\right)_y = \left(\frac{\partial^2 z}{\partial x^2}\right)_y = 6$$

We can also differentiate with respect to x first and y second:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial^2 f}{\partial y \partial x}\right) = 2$$

> Check the videos below if you are learning this for the first time, or if you feel you need to refresh the concept of partial derivatives.
>
> - Partial derivatives: http://patrickjmt.com/derivatives-finding-partial-derivatives (don't get confused by the different notation!)
> - Partial derivatives: http://www.youtube.com/watch?v=vxJR5graUfI
> - Higher order partial derivatives: http://www.youtube.com/watch?v=3itjTS2Y9oE

If a function of two or more variables and its derivatives are single-valued and continuous, a property normally attributed to physical variables, then the mixed partial second derivatives are equal (Euler reciprocity):

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right) \tag{8.1.1}$$

For example, for $z = 3x^2 - y^2 + 2xy$:

$$\left(\frac{\partial^2 f}{\partial y \partial x}\right) = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial y}(6x+2y)\right)_x = 2$$

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial}{\partial x}(-2y+2x)\right)_y = 2$$

Another useful property of the partial derivatives is the so-called reciprocal identity, which holds when the same variables are held constant in the two derivatives:

$$\left(\frac{\partial y}{\partial x}\right) = \frac{1}{\left(\frac{\partial x}{\partial y}\right)} \tag{8.1.2}$$

For example, for $z = x^2y$:

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial}{\partial x}x^2y\right)_y = 2xy$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2} = \frac{1}{2xy} = \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

Finally, let's mention the cycle rule. For a function $z(x,y)$:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \tag{8.1.3}$$

We can construct other versions as follows:

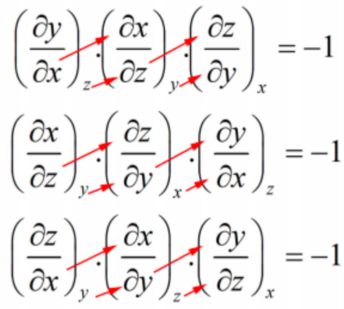


Figure 8.1.3: The chain rule: Start with any partial derivative, and follow the pattern to construct the rest (CC BY-NC-SA; Marcia Levitus)

For example, for $z = x^2 y$:

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial}{\partial x}(z/x^2)\right)_z = -2z/x^3$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial}{\partial z}\sqrt{z/y}\right)_y = \frac{1}{2y}(z/y)^{-1/2}$$

$$\left(\frac{\partial z}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}x^2 y\right)_x = x^2$$

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -\frac{2z}{x^3}\frac{1}{2y}\left(\frac{y}{z}\right)^{1/2} x^2 = -\left(\frac{z}{y}\right)^{1/2}\frac{1}{x} = -\left(\frac{x^2 y}{y}\right)^{1/2}\frac{1}{x} = -1$$

Before discussing partial derivatives any further, let's introduce a few physicochemical concepts to put our discussion in context.

8.2: The Equation of State

Note

From the last section, the cycle rule is defined as follows:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \tag{8.2.1}$$

The thermodynamic state of a system, such as a fluid, is defined by specifying a set of measurable properties sufficient so that all remaining properties are determined. For example, if you have a container full of a gas, you may specify the pressure, temperature and number of moles, and this should be sufficient for you to calculate other properties such as the density and the volume. In other words, the temperature (T), number of moles (n), volume (V) and pressure (P) are not all independent variables.

Ideal Gas Equation of State

To make sense of this statement, let's consider an ideal gas. You know from your introductory chemistry courses[1] that temperature, number of moles, volume and pressure are related through a universal constant R:

$$P = \frac{nRT}{V} \tag{8.2.2}$$

If P is expressed in atmospheres, V in liters, and T in Kelvin, then $R = 0.082\ \frac{L\times atm}{K\times mol}$

This expression tells you that the four variables cannot be changed independently. If you know three of them, you also know the fourth.

Equation 8.2.2 is one particular case of what is known as an **equation of state**. An equation of state is an expression relating the density of a fluid with its temperature and pressure. Note that the density is related to the number of moles and the volume, so it takes care of these two variables together. There is no single equation of state that predicts the behavior of all substances under all conditions. Equation 8.2.2, for example, is a good approximation for non polar gases at low densities (low pressures and high temperatures). Other more sophisticated equations are better suited to describe other systems in other conditions, but there is no universal equation of state.

In general, for a simple fluid, an equation of state will be a relationship between P and the variables T, V and n:

$$P = P(T, V, n) = P(T, V_m),$$

where V_m is the molar volume, V/n. The molar volume is sometimes written as $\bar{V}$. For example, Equation 8.2.2 can be rerwritten as

$$P = \frac{RT}{\bar{V}}.$$

Let's 'play' with the equation of state for an ideal gas. The partial derivative $\left(\frac{\partial P}{\partial T}\right)_{V,n}$ represents how the pressure changes as we change the temperature of the container at constant volume and constant n:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V}$$

It is a relief that the derivative is positive, because we know that an increase in temperature causes an increase in pressure! This also tells us that if we increase the temperature by a small amount, the increase in pressure will be larger in a small container than in a large container.

The partial derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ represents how the pressure changes as we change the volume of the container at constant temperature and constant n:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = -\frac{nRT}{V^2}$$

Again, we are happy to see the derivative is negative. If we increase the volume we should see a decrease in pressure as long as the temperature is held constant. This is not too different from squeezing a balloon (don't try this at home!).

We can also write an equation that represents how the volume changes with a change in pressure: $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. From Equation 8.2.2,

$$V = \frac{nRT}{P}$$

and therefore:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = -\frac{nRT}{P^2}$$

Let's compare these two derivatives:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = -\frac{nRT}{P^2} = -\frac{nRT}{(nRT/V)^2} = -\frac{V^2}{nRT} = \frac{1}{\left(\frac{\partial P}{\partial V}\right)_{T,n}}$$

Surprised? You shouldn't be based on the inverse rule! (Equation ???). Note that this works because we hold the same variables constant in both cases.

Now, you may argue that the inverse rule is not particularly useful because it doesn't take a lot of work to solve for V and perform $\left(\frac{\partial V}{\partial P}\right)_{T,n}$.

Dieterici's Equation of State

Let's consider a more complex equation of state known as Dieterici's equation of state for a real gas:

$$P = \frac{RT}{\bar{V} - b} e^{-a/(R\bar{V}T)}$$

Here, a and b are constants that depend on the particular gas (e.g. whether we are considering $\mathrm{H_2}$ or $\mathrm{CO_2}$). Let's say you are asked to obtain $\left(\frac{\partial V}{\partial P}\right)_{T,n}$. What do you do? Do you find the inverse rule useful now?

Let's go back to the ideal gas, and calculate other partial derivatives:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n} = -\frac{nRT}{V^2} \tag{8.2.3}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{P} \tag{8.2.4}$$

$$\left(\frac{\partial T}{\partial P}\right)_{V,n} = \frac{V}{nR} \tag{8.2.5}$$

Let's calculate the product:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial P}\right)_{V,n} = -\frac{nRT}{V^2}\frac{nR}{P}\frac{V}{nR} = -\frac{nRT}{VP} = -1$$

In the last step, we used Equation 8.2.2. Surprised? You shouldn't be based on the cycle rule! (Equation 8.2.1). Again, this is not particularly useful for an ideal gas, but let's think about Dieterici's equation again and let's assume that you are interested in calculating $\left(\frac{\partial V}{\partial T}\right)_{P,n}$. What would you do?

8.3: The Chain Rule

We all know that the position of a point in space can be specified with two coordinates, x and y, called the cartesian coordinates. We also know that we can choose instead to specify the position of the point using the distance from the origin (r) and the angle that the vector makes with the x axis (θ). The latter are what we call plane polar coordinates, which we will cover in much more detail in Chapter 10.

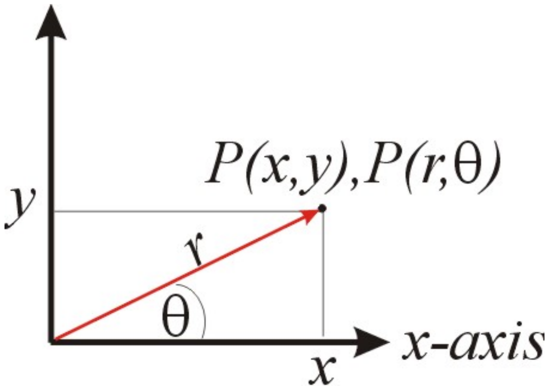


Figure 8.3.1: Cartesian and polar coordinates. (CC BY-NC-SA; Marcia Levitus)

The two coordinate systems are related by:

$$x = r\cos\theta; \quad y = r\sin\theta \tag{8.3.1}$$

$$r = \sqrt{x^2+y^2}; \quad \theta = tan^{-1}(y/x) \tag{8.3.2}$$

Let's assume that we are given a function in polar coordinates, for example $f(r,\theta) = e^{-3r}\cos\theta$, and we are asked to find the partial derivatives in cartesian coordinates, $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$. We can of course re-write the function in terms of x and y and find the derivatives we need, but wouldn't it be wonderful if we had a universal formula that converts the derivatives in polar coordinates ($(\partial f/\partial r)_\theta$ and $(\partial f/\partial \theta)_r$) to the derivatives in cartesian coordinates? This would allow us to take the derivatives in the system the equation is expressed in (which is easy), and then translate the derivatives to the other system without thinking too much. The chain rule will allow us to create these 'universal ' relationships between the derivatives of different coordinate systems.

Before using the chain rule, let's obtain $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$ by re-writing the function in terms of x and y. I want to show you how much work this would involve, so you can appreciate how useful using the chain rule is. Using Equations 8.3.1 and 8.3.2, we can rewrite $f(r,\theta) = e^{-3r}\cos\theta$ as

$$f(x,y) = \frac{e^{-3(x^2+y^2)^{1/2}}x}{(x^2+y^2)^{1/2}}$$

We can easily obtain $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$, but it is certainly quite a bit of work. What if I told you that $(\partial f/\partial x)_y$ is simply

$$\left(\frac{\partial f}{\partial x}\right)_y = \cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta - \frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \tag{8.3.3}$$

independently of the function f? We will derive this result shortly, but for now let me just mention that the procedure involves using the chain rule. You are probably sighing in relief, because the derivatives $(\partial f/\partial r)_\theta$ and $(\partial f/\partial \theta)_r$ are much easier to obtain:

$$\left(\frac{\partial f}{\partial r}\right)_\theta = -3e^{-3r}\cos\theta$$

$$\left(\frac{\partial f}{\partial \theta}\right)_r = -e^{-3r}\sin\theta$$

and using Equation 8.3.3, we can obtain the derivative we are looking for:

$$\left(\frac{\partial f}{\partial x}\right)_y = -\cos\theta \times 3e^{-3r}\cos\theta + \frac{\sin\theta}{r}e^{-3r}\sin\theta$$

$$\left(\frac{\partial f}{\partial x}\right)_y = -\cos^2\theta \times 3e^{-3r} + \frac{\sin^2\theta}{r}e^{-3r} = e^{-3r}\left(\frac{\sin^2\theta}{r} - 3\cos^2\theta\right)$$

$$\left(\frac{\partial f}{\partial x}\right)_y = e^{-3(x^2+y^2)^{1/2}}\left(\frac{y^2}{(x^2+y^2)^{3/2}} - 3\frac{x^2}{(x^2+y^2)}\right)$$

Hopefully this wasn't too painful, or at least, less tedious that it would have been hadn't we used the chain rule. What about $(\partial f/\partial y)_x$? We can create an expression similar to Equation 8.3.3 and use it to relate $(\partial f/\partial y)_x$ with $(\partial f/\partial r)_\theta$ and $(\partial f/\partial \theta)_r$.

At this point you may be thinking that this all worked well because the function we had was easier to derive in polar coordinates than in cartesian coordinates. True, but this is the whole point. Many physical systems are described in polar coordinates more naturally than in cartesian coordinates (especially in three dimensions). This has to do with the symmetry of the system. For an atom, for example, it is much more natural to use spherical coordinates than cartesian coordinates. We could use cartesian, but the expressions would be much more complex and hard to work with. If we have equations that are more easily expressed in polar coordinates, getting the derivatives in polar coordinates will always be easier. But why would we want the derivatives in cartesian coordinates then? A great example is the Schrödinger equation, which is at the core of quantum mechanics. We will talk more about this when we discuss operators, but for now, the Schrödinger equation is a partial differential equation (unless the particle moves in one dimension) that can be written as:

$$E\psi(\vec{r}) = -\frac{\hbar}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})$$

Because of the symmetry of the system, for atoms and molecules it is simpler to express the position of the particle ($\vec{r}$) in spherical coordinates. However, the operator ∇^2 (known as the Laplacian) is defined in cartesian coordinates as:

$$\nabla^2 f(x,y,z) = \left(\frac{\partial^2 f}{\partial x^2}\right)_{y,z} + \left(\frac{\partial^2 f}{\partial y^2}\right)_{x,z} + \left(\frac{\partial^2 f}{\partial z^2}\right)_{x,y}$$

In other words, the Laplacian instructs you to take the second derivatives of the function with respect to x, with respect to y and with respect to z, and add the three together. We could express the functions $V(\vec{r})$ and $\psi(\vec{r})$ in cartesian coordinates, but again, this would lead to a terribly complex differential equation. Instead, we can express the Laplacian in spherical coordinates, and this is in fact the best approach. To do this, we would need to relate the derivatives in spherical coordinates to the derivatives in cartesian coordinates, and this is done using the chain rule.

Hopefully all this convinced you of the uses of the chain rule in the physical sciences, so now we just need to see how to use it for our purposes. In two dimensions, the chain rule states that if we have a function in one coordinate system $u(x,y)$, and these coordinates are functions of two other variables (e.g. $x = x(\theta, r)$ and $y = y(\theta, r)$) then:

$$\left(\frac{\partial u}{\partial r}\right)_\theta = \left(\frac{\partial u}{\partial x}\right)_y\left(\frac{\partial x}{\partial r}\right)_\theta + \left(\frac{\partial u}{\partial y}\right)_x\left(\frac{\partial y}{\partial r}\right)_\theta$$

$$\left(\frac{\partial u}{\partial \theta}\right)_r = \left(\frac{\partial u}{\partial x}\right)_y\left(\frac{\partial x}{\partial \theta}\right)_r + \left(\frac{\partial u}{\partial y}\right)_x\left(\frac{\partial y}{\partial \theta}\right)_r$$

Some students find the following 'tree' constructions useful:

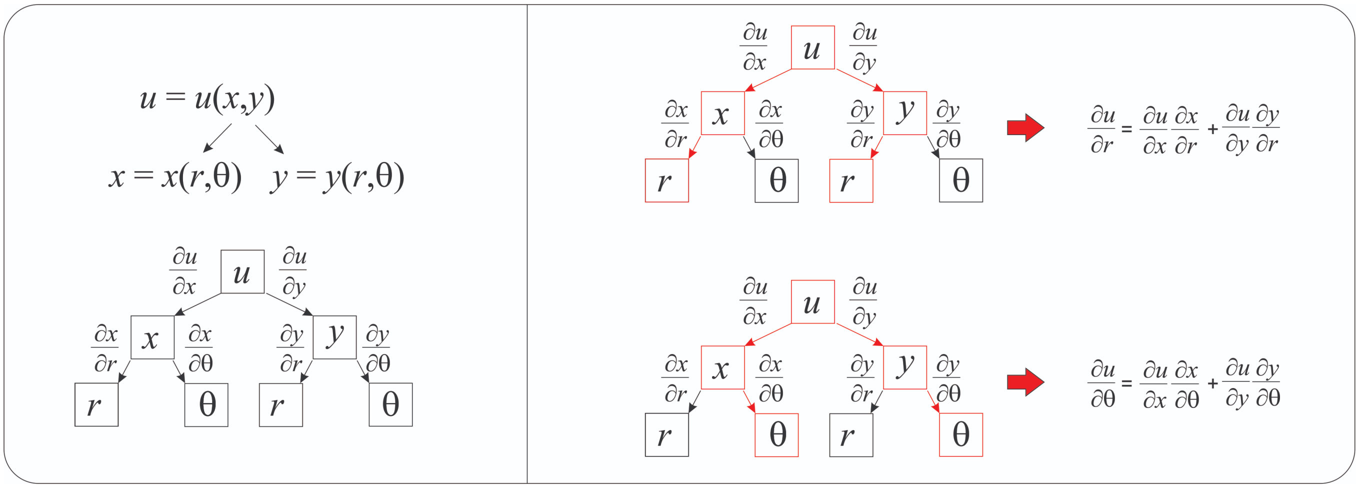


Figure 8.3.2: The chain rule (CC BY-NC-SA; Marcia Levitus)

We can also consider $u=u(r,\theta)$, and $\theta=\theta(x,y)$ and $r=r(x,y)$, which gives:

$$\left(\frac{\partial u}{\partial x}\right)_y=\left(\frac{\partial u}{\partial r}\right)_\theta\left(\frac{\partial r}{\partial x}\right)_y+\left(\frac{\partial u}{\partial \theta}\right)_r\left(\frac{\partial \theta}{\partial x}\right)_y$$

$$\left(\frac{\partial u}{\partial y}\right)_x=\left(\frac{\partial u}{\partial r}\right)_\theta\left(\frac{\partial r}{\partial y}\right)_x+\left(\frac{\partial u}{\partial \theta}\right)_r\left(\frac{\partial \theta}{\partial y}\right)_x$$

Example 8.3.1

Derive Equation 8.3.3.

Solution

We need to prove $\left(\frac{\partial f}{\partial x}\right)_y=\cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta-\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$. Using the chain rule:

$$\left(\frac{\partial f}{\partial x}\right)_y=\left(\frac{\partial f}{\partial \theta}\right)_r\left(\frac{\partial \theta}{\partial x}\right)_y+\left(\frac{\partial f}{\partial r}\right)_\theta\left(\frac{\partial r}{\partial x}\right)_y$$

From Equation 8.3.1 and 8.3.2

$$\left(\frac{\partial r}{\partial x}\right)_y=\frac{1}{2}(x^2+y^2)^{-1/2}(2x)=\frac{1}{2}(r^2)^{-1/2}(2r\cos\theta)=\cos\theta$$

$$\left(\frac{\partial \theta}{\partial x}\right)_y=\frac{1}{1+(y/x)^2}\frac{(-y)}{x^2}=-\frac{1}{1+(y/x)^2}\frac{y}{x}\frac{1}{x}=-\frac{1}{1+\tan^2\theta}\tan\theta\frac{1}{r\cos\theta}=-\frac{1}{1+\frac{\sin^2\theta}{\cos^2\theta}}\frac{\sin\theta}{\cos\theta}\frac{1}{r\cos\theta}=-\frac{\sin\theta}{r}$$

Therefore,

$$\left(\frac{\partial f}{\partial x}\right)_y=\cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta-\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r$$

Need help? The videos below contain examples of how to use the chain rule for partial derivatives:

- Example 1: http://www.youtube.com/watch?v=HOYA0-pOHsg
- Example 2: http://www.youtube.com/watch?v=kCr13iTRN7E (tree diagrams)

8.4: Double and Triple Integrals

We can extend the idea of a definite integral to more dimensions. If $f(x,y)$ is continuous over the rectangle $R=[a,b]\times[c,d]$ then,

$$\iint_R f(x,y)dA=\int_a^b\int_c^d f(x,y)\,dy\,dx=\int_c^d\int_a^b f(x,y)\,dx\,dy \tag{8.4.1}$$

If $f(x,y)\geq 0$, then the double integral represents the volume V of the solid that lies above the rectangle R and below the surface $z=f(x,y)$ (Figure $8.4.1$).

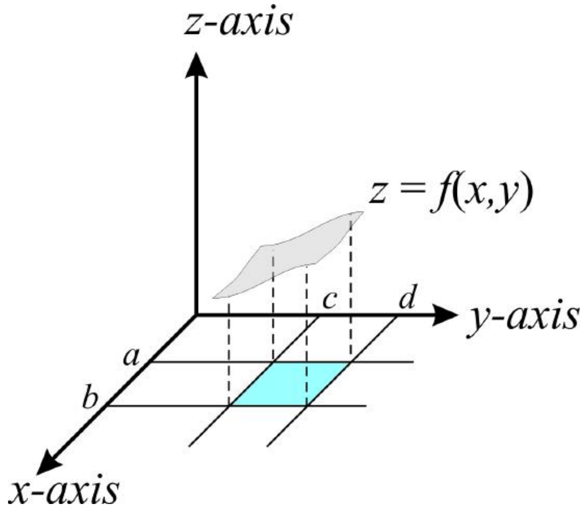


Figure $8.4.1$: Geometric interpretation of a double integral (CC BY-NC-SA; Marcia Levitus)

We can compute the double integral of Equation $8.4.1$ as:

$$\iint_R f(x,y)dA=\int_a^b\left[\int_c^d f(x,y)\,dy\right]dx$$

meaning that we will first compute

$$\int_c^d f(x,y)\,dy$$

holding x constant and integrating with respect to y. The result will be a function containing only x, which we will integrate between a and b with respect to x.

For example, let's solve $\int_0^3\int_1^2 x^2y\;dy\;dx$. We'll start by solving $\int_1^2 x^2y\;dy$ holding x constant:

$$\int_1^2 x^2y\;dy=x^2\int_1^2 y\;dy=\frac{3}{2}x^2$$

Now we integrate this function from 0 to 3 with respect to x:

$$\int_0^3\int_1^2 x^2y\;dy\;dx=\int_0^3\frac{3}{2}x^2\;dx=\frac{27}{2}$$

You can of course integrate from 0 to 3 first with respect to x holding y constant, and then integrate the result with respect to y from 1 to 2. Try it this way and verify you get the same result.

Triple integrals work in the same way. If $f(x,y,z)$ is continuous on the rectangular box $B=[a,b]\times[c,d]\times[r,s]$, then

$$\iiint_B f(x,y,z)dV=\int_r^s\int_c^d\int_a^b f(x,y)\,dx\,dy\,dz \tag{8.4.2}$$

This iterated integral means that we integrate first with respect to x (keeping y and z fixed), then we integrate with respect to y (keeping z fixed), and finally we integrate with respect to z. There are five other possible orders in which we can integrate, all of which give the same value.

> Do you need a refresher on double and triple integrals? Check the videos below before moving on to the physical chemistry examples.
>
> - Example 1: http://www.youtube.com/watch?v=RqD89-afGS0
> - Example 2: http://www.youtube.com/watch?v=CPR0ZD0IYVE (check the example that starts around 3:45 min. and ends at 5:07 min)

Triple integrals are used very often in physical chemistry to normalize probability density functions. For example, in quantum mechanics, the absolute square of the wave function, $|\psi(x,y,z)|^2$, is interpreted as a *probability density*, the probability that the particle is inside the volume $dx.dy.dz$. Since the probability of finding the particle somewhere in space is 1, we require that:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz=1 \tag{8.4.3}$$

We already mentioned wave functions in Section 2.3, where we showed that

$$|\psi(x,y,z)|^2=\psi^*(x,y,z)\psi(x,y,z)$$

The normalization condition, therefore, can also be written as

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*\psi\,dx\,dy\,dz=1 \tag{8.4.4}$$

Example 8.4.1

In quantum mechanics, the lowest energy state of a particle confined in a three-dimensional box is represented by

$$\psi(x,y,z)=A\sin\frac{\pi x}{a}\sin\frac{\pi y}{b}\sin\frac{\pi z}{c}\ if\ \begin{cases}0<x<a\\0<y<b\\0<z<c\end{cases}$$

and

$$\psi(x,y,z)=0 \text{ otherwise (outside the box).}$$

Here, A is a normalization constant, and a,b and c are the lengths of the sides of the box. Since the probability of finding the particle somewhere in space is 1, we require that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz=1$$

Find the normalization constant A in terms of a,b,c and other constants.

Solution

Because $\psi(x,y,z)=0$ outside the box,

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi(x,y,z)|^2\,dx\,dy\,dz=\int_0^c\int_0^b\int_0^a|\psi(x,y,z)|^2\,dx\,dy\,dz=|\psi(x,y,z)|^2=\psi^*(x,y,z)\psi(x,y,z)$$

However, because in this case the function is real,

$$|\psi(x,y,z)|^2=(\psi(x,y,z))^2$$

$$\int_0^c\int_0^b\int_0^a|\psi(x,y,z)|^2\,dx\,dy\,dz=\int_0^c\int_0^b\int_0^a A^2\sin^2\left(\frac{\pi x}{a}\right)\sin^2\left(\frac{\pi y}{b}\right)\sin^2\left(\frac{\pi z}{c}\right)\,dx\,dy\,dz=1$$

$$\int_0^c\int_0^b\int_0^a A^2\sin^2\left(\frac{\pi x}{a}\right)\sin^2\left(\frac{\pi y}{b}\right)\sin^2\left(\frac{\pi z}{c}\right)dx\;dy\;dz=A^2\int_0^a\sin^2\left(\frac{\pi x}{a}\right)dx\int_0^b\sin^2\left(\frac{\pi y}{b}\right)dy\int_0^c\sin^2\left(\frac{\pi z}{c}\right)dz$$

Using the formula sheet, we get

$$\int_0^a\sin^2\left(\frac{\pi x}{a}\right)dx=a/2$$

And therefore,

$$A^2\int_0^a\sin^2\left(\frac{\pi x}{a}\right)dx\int_0^b\sin^2\left(\frac{\pi y}{b}\right)dy\int_0^c\sin^2\left(\frac{\pi z}{c}\right)dz=A^2\frac{a}{2}\frac{b}{2}\frac{c}{2}=\frac{A^2abc}{8}=1$$

Solving for A:

$$A=\left(\frac{8}{abc}\right)^{1/2}$$

8.5: Real Gases

So far in this chapter, most of you have not learned anything that you have not learned in your calculus courses. The math in this chapter is actually pretty easy, but yet, it is common that students find it very hard to apply these mathematical tools to actual problems in the physical sciences. To get you comfortable using math in chemistry we will first learn a little bit about gases and thermodynamics. Having some background will help us use the math in a context that we (chemists) can relate to.

We have already mentioned some thermodynamic variables, but in order to make more connections between chemistry and math we need to introduce some concepts that we need to start discussing real gases. You will talk about these concepts in more depth in CHM 346. An important thermodynamic variable that is used to characterize the state of a system is the internal energy (U). Let's think about a container containing a gas (e.g. O_2). The internal energy of the system is the sum of the following contributions:

- Kinetic energy: The kinetic energy is the energy that the molecules have due to their motions. It is related to their velocity, and as expected, it increases with increasing temperature, as molecules move faster.
- Vibrational and rotational energy: Molecules store energy in their bonds. As we already discussed, atoms vibrate around their equilibrium position, and there is an energy associated with these vibrations. The vibrational energy of a molecule also depends on temperature, and on the number of bonds. Atomic gases (He, Ar, etc) do not have vibrational energy. Molecules also rotate, and there is energy stored in these motions. As in the case of vibrations, atomic gases do not have contributions from rotations. You will learn about vibrational and rotational energy in CHM 345.
- Potential energy: This is the energy due to the interactions between the molecules that make up the gas. Atoms (e.g. Ar) will also interact if brought close enough. The energy of the interactions between the molecules depends obviously on the chemical nature of the molecules. We know that polar molecules will interact more strongly than non-polar molecules, and atoms with more electrons (e.g. Ar) will interact more strongly than atoms of low atomic number (e.g. He). For a given gas, these interactions depend on the distance between the molecules.

For simplicity, we will concentrate on atomic gases, where the only contributions to U are the kinetic energy (which depends on temperature only), and potential energy. You already learned about the simplest model used to describe the behavior of gases: the ideal (or perfect) gas. You learned that there are two assumptions behind the model. First the particles do not have any size, meaning that you can push them together as close as you want. In reality, atoms have a size, and if you try to push them together too hard the electronic clouds will repel each other. The other assumption is that particles do not interact with each other at any distance. In reality, this makes sense only at very low densities, when molecules are very far away from each other. However, as molecules get closer together, they experience attractive forces that in many cases are so strong that result in the formation of a liquid. Of course if we push them too close the forces become repulsive, but there is a range of distances in which attractive forces dominate. This makes sense for polar molecules, but what about atoms (e.g. Ar), that do not have a permanent dipole moment? You probably heard about London dispersive forces, without which we would never be able to liquefy a noble gas. London forces are stronger for atoms containing more electrons, and that is why the boiling point of Xe is much higher than the boiling point of Ne.

With all this in mind, let's think about what happens to an ideal gas in the three situations depicted in Figure $8.5.1$. The densities (molecules per unit volume) increase as we increase the pressure applied to the container. Let's assume the three containers are equilibrated at the same temperature, and let's think about how the internal energy compares among the three cases. We do not have any equations yet, so we need to think in terms of the concepts we just discussed. We have two contributions to think about. The kinetic term should be the same in the three containers because the temperature is the same, and that is the only factor that determines the velocity of the molecules. What about the potential energy? The particles do not have a size, so there are no repulsive forces that arise if we try to push them together too close. They do not have any type of attractive interactions either, so an ideal gas does not store any potential energy. We just concluded that the internal energy for an ideal gas equals the kinetic energy, and it is therefore a function of the temperature of the gas, but not its density. Now, we know that ideal gases are simplified representations of real gases, but they do not exist. In which of these three situations is a gas more likely to behave as an ideal gas? Clearly, when the density is low, the molecules are further away, the interactions between them are weaker, and we do not need to worry about potential energy much.

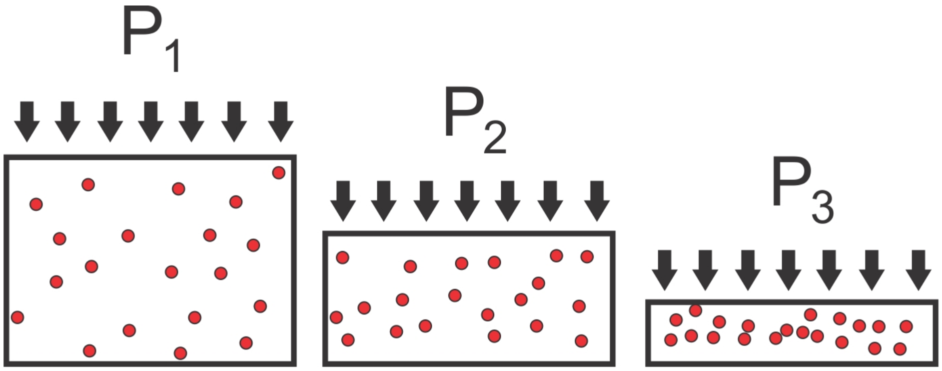


Figure 8.5.1: The internal energy of gases (CC BY-NC-SA; Marcia Levitus)

The van der Waals Model

Let’s come back to the equation of state of an ideal gas 8.5.1:

$$P=\frac{nRT}{V} \tag{8.5.1}$$

In order to improve our description of gases we need to take into account the two factors that the ideal gas model neglects: the size of the molecules, and the interactions between them. The size of the molecules can be taken into account by assuming that the volume that the molecules have to move around is not really V, but instead $V-nb$, where nb is a measure of the volume that the molecules occupy themselves. In this context b is a measure of the volume of one molecule, so nb takes into account the volume of all molecules present in the gas. This first correction gives:

$$P=\frac{nRT}{V-nb} \tag{8.5.2}$$

which is known as the ‘hard spheres’ model. note that we have not introduced anything regarding interactions yet, so this model tells us that we can increase the density as much as we want without changing the internal energy until we get to the point where the spheres touch each other. Because they are ‘hard’, the force required to reduce the volume any further would be infinitely large (not too different from pushing a billiard ball inside another one). Translated into potential energy, this means that the potential energy will jump to infinity when the distance between the center of the particles equals two times their radius. This is better than nothing, but not entirely realistic. In reality molecules are not completely hard, and can be pushed against each other a little bit without an infinite force.

What about interactions? We discussed that at moderate densities, attractive interactions dominate over repulsive interactions. In order to incorporate a correction due to attractive interactions we need to recognize that the pressure of the gas needs to be smaller than the pressure of a gas without attractions (like the hard spheres model). The pressure of a gas is a measure of the collisions of the molecules with the walls of the container. Attractive forces should decrease this frequency, so the resulting pressure should be lower:

$$P=\frac{nRT}{V-nb}-C$$

where C will be a positive term, that takes into account the attractive interactions. What should this term depend on? Clearly on the chemical nature of the molecules, and should be larger for atoms with more electrons (e.g. Xe) than for atoms with less electrons (e.g. He). In addition, it should depend on the density of the gas (n/V), as attractive forces are stronger the closer the molecules are. Van der Waals proposed the following equation that satisfies everything we just said:

$$P=\frac{nRT}{V-nb}-a\left(\frac{n}{V}\right)^2 \tag{8.5.3}$$

Check the following examples of van der Waals constants, and see if you understand how the values of a and b make sense in terms of the sizes of the molecules, and what you know about chemical interactions from your general chemistry courses. Pay attention to the units as well.

gas	$a(L^2bar/mol^2)$	$b(L/mol)$

gas	$a(L^2 bar/mol^2)$	$b(L/mol)$
He	0.035	0.0237
Ar	1.35	0.0320
Kr	2.349	0.0398
H_2	0.248	0.02661
O_2	1.378	0.03183
H_2O	5.536	0.03049
CO_2	3.64	0.0427

It is worth stressing that the van der Waals model is still a model, that is, it is not the exact representation of a real gas. It improves many of the deficiencies of the real gas law, but it is still a model.

Coming back to Figure $8.5.1$, imagine now that the containers are filled with a van der Waals gas. The three states have different internal energy now, because the density of the molecules is different, and that changes the forces between them. The potential energy is zero if the molecules are too far for any attractive or repulsive force to be significant, or when the attractive and repulsive forces exactly cancel each other. When attractive forces dominate we would need to exert work to separate the molecules, and the potential energy is negative. When repulsive forces dominate the potential energy is positive, and we would need to exert work to push the molecules closer. With all this in mind, in which of the three situations is the potential energy lower? The answer is container number 3. Molecules are closer (but not close enough to touch each other), so attractive forces are stronger than in container number 1. Attractive forces lower that internal energy of the system. These arguments allow us to plot the potential energy for a van der Waals gas as a function of the distance between the center of the molecules:

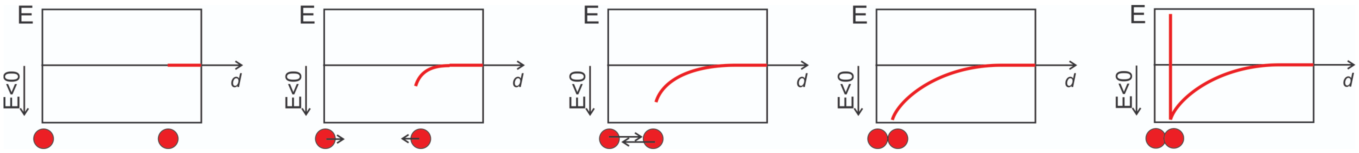


Figure $8.5.2$: The potential energy (E) of a van der Waals gas as two atoms or molecules are brought to close proximity (CC BY-NC-SA; Marcia Levitus)

The potential energy is zero when the distance between molecules is much longer than their diameters. If we start decreasing the density they get closer, and the attractive interactions become significant, lowering the internal energy. This continues until they touch each other. Because they are 'hard spheres' they cannot penetrate each other at all, and the potential energy jumps to infinity. This is equivalent to saying that the force required to push them closer together is infinitely large.

We discussed the difference between a real gas and a model of a real gas. How does this plot look like in reality, and how different is it from the van der Waals model? Below are examples for different gases. Notice that 'Ar_2' does not refer to a gas made up of molecules of Ar_2, but instead to the interactions between two Ar atoms. All the gases in this figure, as we know, are monoatomic.

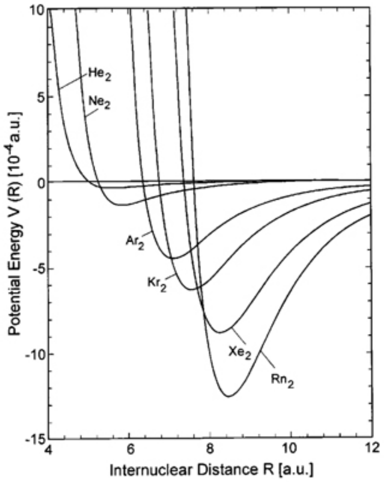


Figure 8.5.3: The potential energy of real gases. (CC BY-NC-SA; Marcia Levitus)

There are a few things worth noting. First, atoms with more electrons (look at a periodic table) show a deeper well. This makes sense because more electrons result in stronger attractive London forces. Also, atoms with more electrons experience these attractive forces at longer distances than atoms with less electrons. In all cases the potential energy increases very sharply when we continue to decrease the distance between the atoms, but the potential energy does not jump to infinity suddenly, as in the case of the van der Waals gas. This means the atoms are not exactly hard spheres. As expected, we can bring two atoms of He much closer than two atoms of Rn before we see these repulsive interactions because atoms of He are much smaller than those of Rn.

Pressure-Volume Isotherms

Scientists started to study the behavior of gases back in the 1600s. As you can imagine, they had very rudimentary laboratory supplies, and their observations were mostly qualitative. One of the earliest quantitative studies in chemistry was performed by Robert Boyle, who noticed that the volume and the pressure of a fixed amount of gas at constant temperature change according to the simple law $P \propto 1/V$, where the symbol "$\propto$" means "proportional to". This is of course true for an ideal gas, whose equation of state is $P = nRT/V$, but not for a real gas. Boyle's law predicts that the volume of a gas decreases as the pressure is increased at constant temperature. Mathematically, this curve is called an hyperbola (hyperbolas are graphs where the product xy is a constant), and physically we call these plots isotherms, because they represent the behavior at constant temperature (*iso* means equal in Latin). In other words, the isotherm for an ideal gas is an hyperbola, but the isotherm for a real gas will show deviations from the hyperbolic shape.

We can of course go to the lab and measure the isotherms for any real gas in any range of temperatures we want. We know that whenever the conditions are such that the density of the gas is low, we expect interactions to be negligible, and therefore isotherms should be very close to the hyperbolas that Boyle described in the 1600s. What happens when interactions are significant? Some experimental isotherms for CO_2 are shown in Figure 8.5.4. At higher temperatures (e.g. 50° C), the isotherm is close to the prediction for an ideal gas: we can compress the volume to small volumes and the pressure will increase following Boyle's law. The isotherms at higher temperatures will be even closer to the hyperbolas predicted by Boyle's law because interactions become less and less noticeable.

What happens at lower temperatures? Let's consider the isotherm at 20° C. Imagine you have a container with one mole of CO_2, and you start reducing its volume at constant temperature. The initial volume is somewhere between 0.5 and 0.6 L (point A in Figure 8.5.4). As you start reducing the volume the pressure starts increasing in approximate agreement with Boyle's law, but notice that important deviations are observed as you approach point B. When the pressure reaches 60 atm (point C), the behavior of the fluid deviates greatly from that predicted by the laws of ideal gases. You continue reducing the volume of the gas, but the pressure not only does not go up as predicted by Boyle's low, but it remains constant for a while (between points C and E)! What is going on? How can we reduce the volume of a gas without increasing the pressure? The answer is that we are not dealing with a pure gas anymore: we are liquefying part of it. As we move from C to E, we increase the amount of liquid and reduce the amount of gas, and the pressure of the system remains constant as long as we have gas and liquid in equilibrium. Of course the more liquid we have the less volume the CO_2 occupies.

As we mentioned before, ideal gases are not supposed to form liquids because in principle, the molecules that make up the gas do not have any size and do not experience any interactions with the other molecules in the container. To form a liquid, molecules need to experience strong attractive forces, or otherwise the motions they experience due to their thermal energy would not allow them to stay close enough. Liquefying a gas, therefore, is a clear experimental evidence of non-ideal behavior and the existence of attractive interactions among molecules.

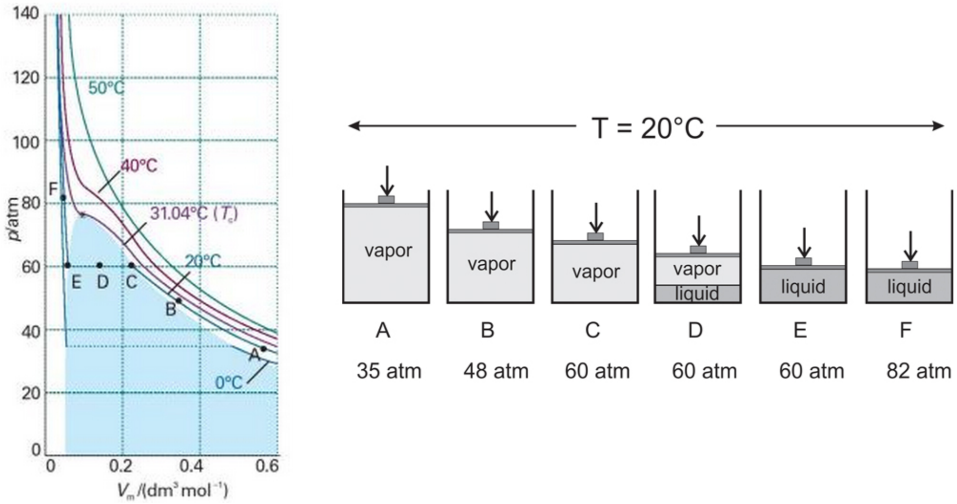


Figure 8.5.4: CO_2 isotherms. (CC BY-NC-SA; Marcia Levitus)

Coming back to Figure $8.5.4$, any point in the horizontal line CDE represents a state where liquid and gas coexist. We call the gas “vapor” in these circumstances, but the distinction is more semantic than physical. When we reach point E, all the CO_2 molecules are part of the liquid. We can continue to reduce the volume, but the pressure of the container will go up much more dramatically than before because we would need to exert a considerable amount of force to push the molecules of liquid closer together. In more technical terms, liquids are much less compressible than gases (see the definition of compressibility in page). The area highlighted in light blue in Figure $8.5.4$ represents the conditions under which CO_2 can exist in equilibrium between the liquid and vapor phases. For example, if we perform the experiment at 0° C, we would start seeing the first drops of liquid when the pressure of the container reaches $\approx$ 35 atm. The pressure will remain constant as we continue to reduce the volume and we form more and more liquid. When no CO_2 remains in the vapor phase, reducing the volume even further would require that we increase the pressure of the container dramatically, as we would be compressing a liquid, not a gas.

Notice that the length of the horizontal line that represents the co-existence of liquid and gas decreases as we increase the temperature. If we were to perform the experiment at 30° C (not shown), we would see that the volume at which we see the first drop of liquid is not too different from the volume at which we stop seeing CO_2 in the gas phase. Liquefying all the gas would require a small change in volume, which means that at that particular temperature and pressure, the volume that the gas occupies is not too different from the volume the liquid occupies. Pretty strange if you think about it...a mole of an ideal gas occupies 22.4L at room temperature, and a mole of liquid water occupies only 18 mL, almost a thousand times less. If we think in terms of densities, the density of water at room temperature is about 1 g/mL, or 0.056 mol/mL. The density of an ideal gas at room temperature is $n/V=P/RT\approx 4\times 10^{-5}$ mol/L, again, around a thousand times less. Yet, at 30° C, and around 80 atm, the density of CO_2 in the liquid state is almost the same as the density of CO_2 in the gas phase. If we put CO_2 in a high pressure cell, and increase P to 80 atm, it would be hard for us to say whether the CO_2 is liquid or gas. At much lower pressures, distinguishing between liquid and gas becomes much more evident, as we are used to from our daily experience.

Critical Behavior

There is a particular isotherm where the CDE line of figure [c2v:fig:isotherms] reduces to a point. In the case of CO_2, this isotherm is the one we measure at 31.04°C, and it is so unique and important that it has a special name: the ‘critical isotherm’. At temperatures below the critical isotherm, we see that the gas condenses to form liquid, and that the pressure of the system remains constant as we convert more and more gas into liquid. The lower the temperature, the more different the densities of the vapor and the liquid are. This is very intuitive for us, because it is what we are used to seeing with the liquid we know best: water. In the case of water, we would need to increase the pressure to 218 atm and work at 374 $^\circ$C to lose our ability to distinguish between liquid water and vapor. The conditions on earth are so far away from the critical point, that we can clearly distinguish liquid water from vapor from their densities. Coming back to CO_2, as we increase the temperature at high pressures (more than 60 atm), the liquid and the vapor states of the fluid become more and more similar. Right below the critical temperature we can hardly distinguish what is liquid and what is vapor, and at exactly the critical temperature, that distinction is lost. Above the critical temperature we never see a separation of phases, we just see a fluid that becomes denser as we reduce the volume of the container. Notice that the critical point is an inflection point in the critical isotherm. This happens at a particular molar volume (for CO_2 $V_c = 0.094$ L/mol) and at a particular pressure (for CO_2 $P_c = 72.9$ atm), which we call the critical molar volume and critical pressure of the fluid. If we want to liquefy CO_2, we need to do it at temperatures below its critical temperature (31.04°C). At temperatures above this value the fluid will always be a gas, although it could be a very dense gas! Chemists call this state ‘supercritical fluid’ just to differentiate it from a low-density gas such as CO_2 at 1 atm. Again, to give you an idea, one mole of CO_2 occupies about 25L at 1 atm and 40°C, and we call it a gas without thinking twice. From figure [c2v:fig:isotherms], at 80 atm and 40° C one mole of CO_2 occupies about 0.15L, about 170 times less than the gas we are used to seeing at 1 atm. This is a very dense fluid, but technically it is not a liquid because we are above the critical temperature. Instead, we use the term supercritical fluid. As it turns out, supercritical CO_2 is much more than a curiosity. It is used as a solvent for many industrial processes, including decaffeinating coffee and dry cleaning.

From our discussion above, it is clear that ideal gases do not display critical behavior. Again, ideal gases do not exist, so when we say that ideal gases do not display critical behavior we are just saying that 1) gases show critical behavior at conditions of temperature, pressure and molar volume that are very far from the conditions where the simple equation $PV = nRT$ describes the behavior of the gas and that 2) if we want to describe a gas close to the critical point we need an equation of state that is consistent with critical behavior. If we plot the isotherms of an ideal gas ($P = nRT/V$) we will obtain hyperbolas a any temperature. Again, this works well with gases at very low densities, but because the model does not include interactions, it cannot possibly describe the isotherms at or around the critical point.

Is the hard spheres model of Equation 8.5.2 consistent with the existence of the critical point? To answer this question, we could plot many isotherms according to this equation and see if the model gives one isotherm that has an inflection point as the one shown in Figure 8.5.4. Once again, keep in mind that the figure contains the data we measure experimentally, which is what CO_2 is actually doing in nature. Equations of state by definition are models that are meant to describe the system as close as possible, but they are by definition simplifications of the real behavior. Coming back to the model of hard spheres, you can plot as many isotherms as you want, but you will see that none of them show an inflection point. This is pretty obvious from the equation, as the isotherms are basically the same we would get with the ideal gas equation, but just shifted in the $x-$axis by the quantity b. Physically speaking, it is not surprising because the hard spheres model does not contain any parameter that accounts for the attractive interactions between molecules, and that is what we need to describe critical behavior.

We know that the van der Waals equation is the simplest equation that introduces a term to account for attractive forces (Equation 8.5.3), so it is likely that his equation might be consistent with critical behavior. Let’s discuss what we mean by this in more detail. Again, van der Waals gases do not exist in nature. They are a theoretical construction where we think about molecules as hard spheres with kinetic energy that interact with each other so that the average interaction between two randomly oriented molecules is inversely proportional to the inverse of the sixth power of the distance between them. If we could create a gas whose molecules followed these exact physical laws, the gas would behave exactly as the van der Waals equation predicts. So, now we wonder: would such a gas show an isotherm with an inflection point like the one shown for the case of real CO_2? The answer is yes, and the critical constants (P_c, T_c and V_c) depend on the values of the van der Waals parameters, a and b.

Now, the fact that the van der Waals model predicts critical behavior does not mean at all that it describes the whole isotherm well. If you plot the van der Waals equation at different temperatures you will see that this model does not predict the “flat ” $P - V$ part of the curve, where the liquid and the gas coexist. This is not surprising, as the treatment of the attractive interactions in the van der Waals model is too simple to describe the liquid state. In fact, you will see that the van der Waals equation predicts that the derivative $\left(\frac{\partial P}{\partial V}\right)_{T,n}$ is positive in certain regions of the isotherm, which of course does not make any physical sense. Compressing the gas will never lower the pressure as the van der Waals gas predicts, so we can clearly see how the model fails when attractive forces are important are complex. In any case, it is pretty impressive to see how such a simple equation predicts such complex behavior as the critical point.

8.6: Problems

? Problem 8.6.1

Given a generic equation of state $P = P(V, T, n)$, explain how you can obtain the derivative

$$\frac{\partial V}{\partial T}_{P,n}$$

using the properties of partial derivatives we learned in this chapter.

? Problem 8.6.2

The thermodynamic equation:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

shows how the internal energy of a system varies with the volume at constant temperature.

Prove that

1. $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas.
2. $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ for one mole of van der Waals gas (Equation 8.6.2)

? Problem 8.6.3

Consider one mole of a van der Waals gas (Equation 8.6.2) and show that

$$\left(\frac{\partial^2 P}{\partial V \partial T}\right) = \left(\frac{\partial^2 P}{\partial T \partial V}\right)$$

? Problem 8.6.4

Consider a van der Waals gas (Equation 8.6.2) and show that

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{\left(P - \frac{n^2 a}{V^2} + \frac{2n^3 ab}{V^3}\right)}$$

Hint: Calculate derivatives that are easier to obtain and use the properties of partial derivatives to get the one the problem asks for. Do not use the answer in your derivation; obtain the derivative assuming you don't know the answer and simplify your expression until it looks like the equation above.

? Problem 8.6.5

From the definitions of expansion coefficient (α) and isothermal compressibility (κ):

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

and

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}$$

prove that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{\alpha}{\kappa}$$

independently of the equation of state used.

Note: A common mistake in this problem is to assume a particular equation of state. Use the cycle rule to find the required relationship independently of any particular equation of state.

Problem 8.6.6

Derive an equation similar to Equation 8.6.1, but that relates

$$\left(\frac{\partial f}{\partial y}\right)_{x}$$

with

$$\left(\frac{\partial f}{\partial r}\right)_{\theta}$$

and

$$\left(\frac{\partial f}{\partial \theta}\right)_{r}$$

Problem 8.6.7

(Extra-credit level)

The expression:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$$

is known as the Laplacian operator in two dimensions.

When applied to a function $f(x,y)$, we get:

$$\nabla^2 f(x,y) = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2}$$

Express ∇^2 in polar coordinates (2D) assuming the special case where $r = a$ is a constant.

Problem 8.6.8

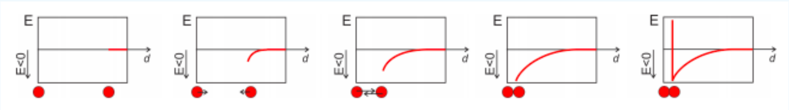
Calculate $\int_0^1 \int_1^2 \int_0^2 \left(x^2 + yz\right)\, dx\, dy\, dz$. Try three different orders of integration an verify you always get the same result.

Problem 8.6.9

Calculate $\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} e^{-r} r^5 \sin\theta\, dr\, d\theta\, d\phi$. Use only the formula sheet.

Problem 8.6.10

How would Figure $8.5.2$, reproduced below, look like for an ideal gas? Sketch the potential energy as a function of the distance between the atoms.



Problem 8.6.11

From everything we learned in this chapter, and without doing any math, we should be able to calculate the sign (>0, <0, or 0) of the following derivatives:

For an ideal gas:

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n}$$

For a van der Vaals gas:

$$\left(\frac{\partial U}{\partial T}\right)_{V,n}$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n}$$

Be sure you can write a short sentence explaining your answers.

Problem 8.6.12

The critical point is the state at which the liquid and gas phases of a substance first become indistinguishable. A gas above the critical temperature will never condense into a liquid, no matter how much pressure is applied. Mathematically, at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}=0$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,n}=0$$

Obtain the critical constants of a van der Waals gas (Equation 8.6.2) in terms of the parameters a and b.

Hint: obtain the first and second derivatives of P with respect to V, make them equal to zero, and obtain T_c and V_c from these equations. Finally, replace these expressions in Equation 8.6.2 to obtain P_c.

Note

As derived in Section 8.3,

$$\left(\frac{\partial f}{\partial x}\right)_y=\cos\theta\left(\frac{\partial f}{\partial r}\right)_\theta-\frac{\sin\theta}{r}\left(\frac{\partial f}{\partial \theta}\right)_r \tag{8.6.1}$$

As defined in Section 8.5, the Van der Waals is defined as:

$$P=\frac{nRT}{V-nb}-a\left(\frac{n}{V}\right)^2 \tag{8.6.2}$$

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1. If you are not familiar with this you need to read about it before moving on

CHAPTER OVERVIEW

9: Exact and Inexact Differentials

Chapter Objectives

- Understand the concept of the total differential
- Understand the concept of exact and inexact differentials.
- Be able to test whether a differential is exact or not.
- Understand how to integrate differentials along different paths.
- Understand the role of exact and inexact differentials in thermodynamics.

9.1: The Total Differential

In Chapter 8 we learned that partial derivatives indicate how the dependent variable changes with one particular independent variable keeping the others fixed. In the context of an equation of state $P = P(T,V,n)$, the partial derivative of P with respect to V at constant T and n is:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

and physically represents how the pressure varies as we change the volume at constant temperature and constant n.

The partial derivative of P with respect to T at constant V and n is:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

and physically represents how the pressure varies as we change the temperature at constant volume and constant n.

What happens with the dependent variable (in this case P) if we change two or more independent variables simultaneously? For an infinitesimal change in volume and temperature, we can write the change in pressure as:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \tag{9.1.1}$$

Equation 9.1.1 is called the *total differential of* P, and it simply states that the change in P is the sum of the individual contributions due to the change in V at constant T and the change in T at constant V. This equation is true for infinitesimal changes. If the changes are not infinitesimal we will integrate this expression to calculate the change in P.[differentials_position1]

Let's now consider the volume of a fluid, which is a function of pressure, temperature and the number of moles: $V = V(n,T,P)$. The total differential of V, by definition, is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,V} dn \tag{9.1.2}$$

If we want to calculate the change in volume in a fluid upon small changes in P, T and n, we could use:

$$\Delta V \approx \left(\frac{\partial V}{\partial T}\right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n}\right)_{T,V} \Delta n \tag{9.1.3}$$

Of course, if we know the function $V = V(n,T,P)$, we could also calculate ΔV as $V_f - F_i$, where the final and initial volumes are calculated using the final and initial values of P, T and n. This seems easy, so why do we need to bother with Equation 9.1.3? The reason is that sometimes we can measure the partial derivatives experimentally, but we do not have an equation of the type $V = V(n,T,P)$ to use. For example, the following quantities are accessible experimentally and tabulated for different fluids and materials (Fig. [fig:diff_tables]):

- $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n}$ (coefficient of thermal expansion)
- $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{V,n}$ (isothermal compressibility)[differentials:compressibility]
- $V_m = \left(\frac{\partial V}{\partial n}\right)_{P,T}$ (molar volume)

Using these definitions, Equation 9.1.2 becomes:

$$dV = \alpha V dT - \kappa V dP + V_m dn \tag{9.1.4}$$

You can find tables with experimentally determined values of α and κ under different conditions, which you can use to calculate the changes in V. Again, as we will see later in this chapter, this equation will need to be integrated if the changes are not small. In any case, the point is that you may have access to information about the derivatives of the function, but not to the function itself (in this case V as a function of T, P, n).

In general, for a function $u = u(x_1, x_2 \ldots x_n)$, we define the total differential of u as:

$$du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2 + \ldots + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n \tag{9.1.5}$$

✓ Example 9.1.1

Calculate the total differential of the function $z = 3x^3 + 3yx^2 + xy^2$.

Solution

By definition, the total differential is:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

For the function given in the problem,

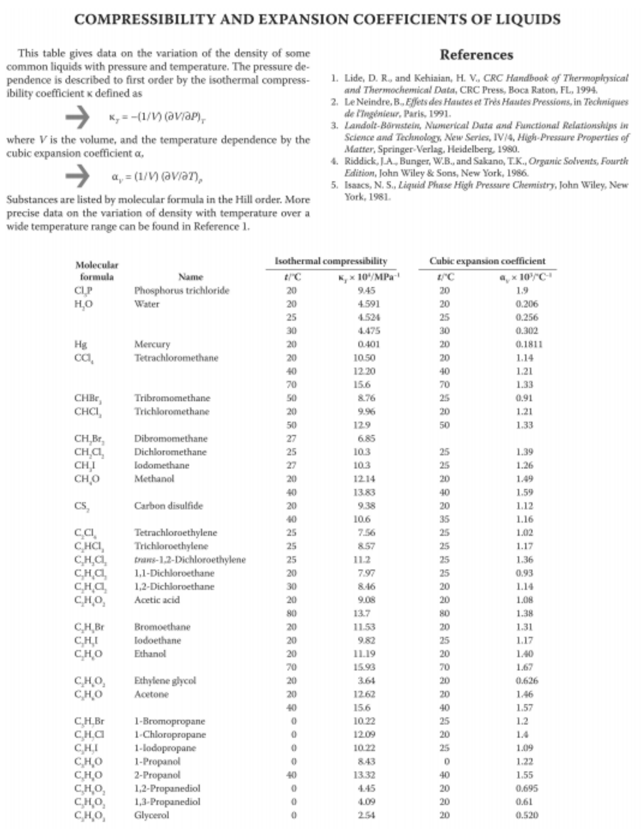
$$\left(\frac{\partial z}{\partial x}\right)_y = 9x^2 + 6xy + y^2$$

and

$$\left(\frac{\partial z}{\partial y}\right)_x = 3x^2 + 2xy$$

and therefore,

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$



COMPRESSIBILITY AND EXPANSION COEFFICIENTS OF LIQUIDS

This table gives data on the variation of the density of some common liquids with pressure and temperature. The pressure dependence is described to first order by the isothermal compressibility coefficient κ defined as

$$\rightarrow \quad \kappa_T = -(1/V)\,(\partial V/\partial P)_T$$

where V is the volume, and the temperature dependence by the cubic expansion coefficient α,

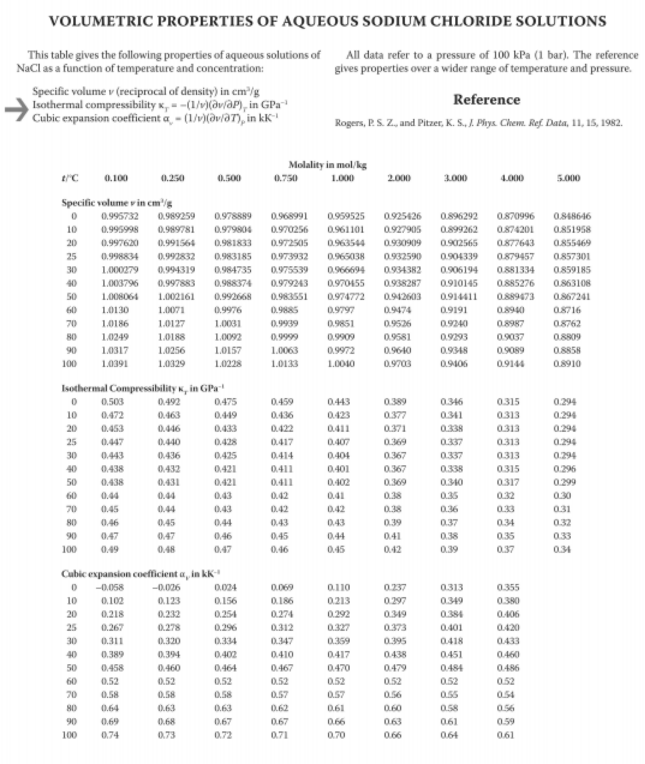
$$\rightarrow \quad \alpha_V = (1/V)\,(\partial V/\partial T)_P$$

Substances are listed by molecular formula in the Hill order. More precise data on the variation of density with temperature over a wide temperature range can be found in Reference 1.

References

1. Lide, D. R., and Kehiaian, H. V., *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Boca Raton, FL, 1994.
2. Le Neindre, B., *Effets des Hautes et Très Hautes Pressions*, in *Techniques de l'Ingénieur*, Paris, 1991.
3. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series*, IV/4, *High-Pressure Properties of Matter*, Springer-Verlag, Heidelberg, 1980.
4. Riddick, J.A., Bunger, W.B., and Sakano, T.K., *Organic Solvents, Fourth Edition*, John Wiley & Sons, New York, 1986.
5. Isaacs, N. S., *Liquid Phase High Pressure Chemistry*, John Wiley, New York, 1981.

Molecular formula	Name	Isothermal compressibility		Cubic expansion coefficient	
		t/°C	$\kappa_T \times 10^4$/MPa^{-1}	t/°C	$\alpha_V \times 10^3$/°C^{-1}
Cl_3P	Phosphorus trichloride	20	9.45	20	1.9
H_2O	Water	20	4.591	20	0.206
		25	4.524	25	0.256
		30	4.475	30	0.302
Hg	Mercury	20	0.401	20	0.1811
CCl_4	Tetrachloromethane	20	10.50	20	1.14
		40	12.20	40	1.21
		70	15.6	70	1.33
$CHBr_3$	Tribromomethane	50	8.76	25	0.91
$CHCl_3$	Trichloromethane	20	9.96	20	1.21
		50	12.9	50	1.33
CH_2Br_2	Dibromomethane	27	6.85		
CH_2Cl_2	Dichloromethane	25	10.3	25	1.39
CH_3I	Iodomethane	27	10.3	25	1.26
CH_4O	Methanol	20	12.14	20	1.49
		40	13.83	40	1.59
CS_2	Carbon disulfide	20	9.38	20	1.12
		40	10.6	35	1.16
C_2Cl_4	Tetrachloroethylene	25	7.56	25	1.02
C_2HCl_3	Trichloroethylene	25	8.57	25	1.17
$C_2H_2Cl_2$	*trans*-1,2-Dichloroethylene	25	11.2	25	1.36
$C_2H_4Cl_2$	1,1-Dichloroethane	20	7.97	25	0.93
$C_2H_4Cl_2$	1,2-Dichloroethane	30	8.46	20	1.14
$C_2H_4O_2$	Acetic acid	20	9.08	20	1.08
		80	13.7	80	1.38
C_2H_5Br	Bromoethane	20	11.53	20	1.31
C_2H_5I	Iodoethane	20	9.82	25	1.17
C_2H_6O	Ethanol	20	11.19	20	1.40
		70	15.93	70	1.67
$C_2H_6O_2$	Ethylene glycol	20	3.64	20	0.626
C_3H_6O	Acetone	20	12.62	20	1.46
		40	15.6	40	1.57
C_3H_7Br	1-Bromopropane	0	10.22	25	1.2
C_3H_7Cl	1-Chloropropane	0	12.09	20	1.4
C_3H_7I	1-Iodopropane	0	10.22	25	1.09
C_3H_8O	1-Propanol	0	8.43	0	1.22
C_3H_8O	2-Propanol	40	13.32	40	1.55
$C_3H_8O_2$	1,2-Propanediol	0	4.45	20	0.695
$C_3H_8O_2$	1,3-Propanediol	0	4.09	20	0.61
$C_3H_8O_3$	Glycerol	0	2.54	20	0.520



VOLUMETRIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

This table gives the following properties of aqueous solutions of NaCl as a function of temperature and concentration:

→ Specific volume v (reciprocal of density) in cm^3/g
Isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial P)_T$ in GPa^{-1}
Cubic expansion coefficient $\alpha_v = (1/v)(\partial v/\partial T)_P$ in kK^{-1}

All data refer to a pressure of 100 kPa (1 bar). The reference gives properties over a wider range of temperature and pressure.

Reference

Rogers, P. S. Z., and Pitzer, K. S., *J. Phys. Chem. Ref. Data*, 11, 15, 1982.

	Molality in mol/kg								
t/°C	0.100	0.250	0.500	0.750	1.000	2.000	3.000	4.000	5.000
Specific volume v in cm^3/g									
0	0.995732	0.989259	0.978889	0.968991	0.959525	0.925426	0.896292	0.870996	0.848646
10	0.995998	0.989781	0.979804	0.970256	0.961101	0.927905	0.899262	0.874201	0.851958
20	0.997620	0.991564	0.981833	0.972505	0.963544	0.930909	0.902565	0.877643	0.855469
25	0.998834	0.992832	0.983185	0.973932	0.965038	0.932590	0.904339	0.879457	0.857301
30	1.000279	0.994319	0.984735	0.975539	0.966694	0.934382	0.906194	0.881334	0.859185
40	1.003796	0.997883	0.988374	0.979243	0.970455	0.938287	0.910145	0.885276	0.863108
50	1.008064	1.002161	0.992668	0.983551	0.974772	0.942603	0.914411	0.889473	0.867241
60	1.0130	1.0071	0.9976	0.9885	0.9797	0.9474	0.9191	0.8940	0.8716
70	1.0186	1.0127	1.0031	0.9939	0.9851	0.9526	0.9240	0.8987	0.8762
80	1.0249	1.0188	1.0092	0.9999	0.9909	0.9581	0.9293	0.9037	0.8809
90	1.0317	1.0256	1.0157	1.0063	0.9972	0.9640	0.9348	0.9089	0.8858
100	1.0391	1.0329	1.0228	1.0133	1.0040	0.9703	0.9406	0.9144	0.8910
Isothermal Compressibility κ_T in GPa^{-1}									
0	0.503	0.492	0.475	0.459	0.443	0.389	0.346	0.315	0.294
10	0.472	0.463	0.449	0.436	0.423	0.377	0.341	0.313	0.294
20	0.453	0.446	0.433	0.422	0.411	0.371	0.338	0.313	0.294
25	0.447	0.440	0.428	0.417	0.407	0.369	0.337	0.313	0.294
30	0.443	0.436	0.425	0.414	0.404	0.367	0.337	0.313	0.294
40	0.438	0.432	0.421	0.411	0.401	0.367	0.338	0.315	0.296
50	0.438	0.431	0.421	0.411	0.402	0.369	0.340	0.317	0.299
60	0.44	0.44	0.43	0.42	0.41	0.38	0.35	0.32	0.30
70	0.45	0.44	0.43	0.42	0.42	0.38	0.36	0.33	0.31
80	0.46	0.45	0.44	0.43	0.43	0.39	0.37	0.34	0.32
90	0.47	0.47	0.46	0.45	0.44	0.41	0.38	0.35	0.33
100	0.49	0.48	0.47	0.46	0.45	0.42	0.39	0.37	0.34
Cubic expansion coefficient α_v in kK^{-1}									
0	−0.058	−0.026	0.024	0.069	0.110	0.237	0.313	0.355	
10	0.102	0.123	0.156	0.186	0.213	0.297	0.349	0.380	
20	0.218	0.232	0.254	0.274	0.292	0.349	0.384	0.406	
25	0.267	0.278	0.296	0.312	0.327	0.373	0.401	0.420	
30	0.311	0.320	0.334	0.347	0.359	0.395	0.418	0.433	
40	0.389	0.394	0.402	0.410	0.417	0.438	0.451	0.460	
50	0.458	0.460	0.464	0.467	0.470	0.479	0.484	0.486	
60	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	
70	0.58	0.58	0.58	0.57	0.57	0.56	0.55	0.54	
80	0.64	0.63	0.63	0.62	0.61	0.60	0.58	0.56	
90	0.69	0.68	0.67	0.67	0.66	0.63	0.61	0.59	
100	0.74	0.73	0.72	0.71	0.70	0.66	0.64	0.61	

Figure 9.1.1: Tables of isothermal compressibilities and expansion coefficients of different fluids (top) and sodium chloride solutions (bottom). Source: CRC Handbook of Physics and Chemistry (CC BY-NC-SA; Marcia Levitus)

> Want to see more examples?
>
> - Example 1: http://www.youtube.com/watch?v=z0TxZ0EHzIg Notice that she calls it ’the differential’, but I prefer ’the total differential’.

9.2: Exact and Inexact Differentials

So far, we discussed how to calculate the total differential of a function. If you are given a function of more than one variable, you can calculate its total differential using the definition of a total differential of a function u: ($du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2 + \ldots + \left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n$). You will have one term for each independent variable. What if we are given a differential (e.g.

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

see Example 9.1) and we are asked to calculate the function whose total differential is dz? This is basically working Example 9.1 backwards: we know the differential, and we are looking for the function. Things are a little bit more complicated than this, because not all differentials are the total differentials of a function. For example, from the example above we know that

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

is the total differential of

$$z(x, y) = 3x^3 + 3yx^2 + xy^2.$$

However, the differential $dz = xydx + x^2dy$ is **not** the total differential of any function $z(x, y)$. You can write down every single function $z(x, y)$ in this planet, calculate their total differentials, and you will never see $dz = xydx + x^2dy$ in your list.

Therefore, the question we are addressing is the following: given a differential, 1) is it the total differential of any function? 2) if it is, which function?

To illustrate the question, let's say we are given the differential below (notice that I switched to P, V, and T, which are variables you will encounter often in thermodynamics):

$$dP = \frac{RT}{V-b} dT + \left[\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right] dV \tag{9.2.1}$$

The question is whether this is the total differential of a function $P = P(T, V)$ (we are told that a and b are constants, and we already know that R is a constant). By definition of total differential, if the function exists, its total differential will be:

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \tag{9.2.2}$$

Comparing Equation 9.2.1 and 9.2.2, if the function exists, its derivatives will have to be:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{RT}{V-b} \tag{9.2.3}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right] \tag{9.2.4}$$

If we find a function $P = P(T, V)$ that satisfies these equations at the same time, we know that Equation 9.2.1 will be its total differential.

From Equation 9.2.3, we can calculate P by integrating with respect to T at constant V:

$$\int dP = \int \frac{RT}{V-b} dT \rightarrow P = \frac{R}{V-b}\frac{T^2}{2} + f(V) \tag{9.2.5}$$

where we included an integration constant ($f(V)$) that can be any function of V (we are integrating at constant V).

In order to get an expression for $P(T, V)$, we need to find out $f(V)$ so we can complete the right side of Equation 9.2.5. To do that, we are going to take the derivative of P (Equation 9.2.5 with respect to V, and compare with Equation 9.2.4:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT^2}{2(V-b)^2} + \frac{df(V)}{dV} \tag{9.2.6}$$

Looking at Equation 9.2.4 and 9.2.6, we see that the two expressions do not match, regardless of which function we chose for $f(V)$. This means that Equation 9.2.1 does not represent the total differential of any function $P(V,T)$. We call these differentials **inexact differentials**. If a differential is the total differential of a function, we will call the differential **exact**.

What we did so far is correct, but it is not the easiest way to test whether a differential is exact or inexact. There is, in fact, a very easy way to test for exactness. We'll derive the procedure below, but in the future we can use it without deriving it each time.

Given the differential $dz = f_1(x,y)dx + f_2(x,y)dy$, the differential is exact if

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y \tag{9.2.7}$$

If Equation 9.2.7 does not hold, the differential is inexact. For instance, if $dz = (9x^2+6xy+y^2)dx + (3x^2+2xy)dy$, the functions f_1 and f_2 are $f_1 = 9x^2+6xy+y^2$ and $f_2 = 3x^2+2xy$. To test this differential, we perform the partial derivatives

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = 6x+2y$$

and

$$\left(\frac{\partial f_2(x,y)}{\partial x}\right)_y = 6x+2y$$

The two derivatives are the same, and therefore the differential is said to be exact.

Let's prove why the test of Equation 9.2.7 works. Let's consider a differential of the form $dz = f_1(x,y)dx + f_2(x,y)dy$. If the differential is exact, it is the total differential of a function $z(x,y)$, and therefore:

$$dz = f_1(x,y)dx + f_2(x,y)dy = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{9.2.8}$$

We know that the mixed partial derivatives of a function are independent of the order they are computed:

$$\left(\frac{\partial^2 z}{\partial y \partial x}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

From Equation 9.2.8,

$$f_1(x,y) = \left(\frac{\partial z}{\partial x}\right)_y \rightarrow \left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

$$f_2(x,y) = \left(\frac{\partial z}{\partial y}\right)_x \rightarrow \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial y \partial x}\right)$$

Because the mixed partial derivatives are the same, for an exact differential:

$$\left(\frac{\partial f_1(x,y)}{\partial y}\right)_x = \left(\frac{\partial f_2(x,y)}{\partial x}\right)_y$$

This equation is true only for an exact differential because we derived it by assuming that the function $z = z(x,y)$ exists, so its mixed partial derivatives are the same. We can use this relationship to test whether a differential is exact or inexact. If the equality of Equation 9.2.7 holds, the differential is exact. If it does not hold, it is inexact.

✓ Example 9.2.1

Test whether the following differential is exact or inexact:

$$dz = \frac{1}{x^2}dx - \frac{y}{x^3}dy$$

Solution

To test whether dz is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(1/x^2)}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial(y/x^3)}{\partial x}\right)_y$$

$$\left(\frac{\partial(1/x^2)}{\partial y}\right)_x = 0$$

$$\left(\frac{\partial(y/x^3)}{\partial x}\right)_y = -3yx^{-4}$$

We conclude that dz is inexact, and therefore there is no function $z(x,y)$ whose total differential is dz.

✓ Example 9.2.2

Determine whether the following differential is exact or inexact. If it is exact, determine $z = z(x,y)$.

$$dz = (2x+y)dx + (x+y)dy$$

Solution

To test whether dz is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(2x+y)}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial(x+y)}{\partial x}\right)_y$$

If this equality holds, the differential is exact.

$$\left(\frac{\partial(2x+y)}{\partial y}\right)_x = 1$$

$$\left(\frac{\partial(x+y)}{\partial x}\right)_y = 1$$

Therefore, the differential is exact. Because it is exact, it is the total differential of a function $z(x,y)$. The total differential of $z(x,y)$ is, by definition,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Comparing this expression to the differential $dz = (2x+y)dx + (x+y)dy$:

$$\left(\frac{\partial z}{\partial x}\right)_y = (2x+y)$$

$$\left(\frac{\partial z}{\partial y}\right)_x = (x+y) \tag{9.2.9}$$

To find $z(x,y)$, we can integrate the first expression partially with respect to x keeping y constant:

$$\int dz = z = \int (2x+y)dx = x^2 + xy + f(y)$$

So far we have

$$z = x^2 + xy + f(y) \tag{9.2.10}$$

so we need to find the function $f(y)$ to complete the expression above and finish the problem. To do that, we'll take the derivative of z with respect to y, and compare with Equation 9.2.9. The derivative of Equation 9.2.10 is:

$$\left(\frac{\partial z}{\partial y}\right)_x = x + \frac{df(y)}{dy}$$

comparing with Equation 9.2.9 we notice that $\frac{df(y)}{dy} = y$, and integrating, we obtain $f(x) = y^2/2 + c$

Therefore, $dz=(2x+y)dx+(x+y)dy$ is the total differential of $z=x^2+xy+y^2/2+c$.

We can check our result by working the problem in the opposite direction. If we are given $z=x^2+xy+y^2/2+c$ and we are asked to calculate its total differential, we would apply the definition:

$$dz=\left(\frac{\partial z}{\partial x}\right)_y dx+\left(\frac{\partial z}{\partial y}\right)_x dy$$

and because

$$\left(\frac{\partial z}{\partial x}\right)_y=y+2x$$

and

$$+\left(\frac{\partial z}{\partial y}\right)_x=y+x$$

we would write $dz=(2x+y)dx+(x+y)dy$, which is the differential we were given in the problem.

Check two extra solved examples in this video: http://tinyurl.com/kq4qecu

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9.3: Differentials in Thermodynamics - State and Path Functions

Distinguishing between exact and inexact differentials has very important consequences in thermodynamics. We already mentioned thermodynamic variables such as the internal energy (U), volume, pressure, and temperature, and you probably heard about entropy (S) and free energy (G). All these quantities can be used to specify the state of a system. They are properties of the current state of the system, and they do not depend on the way the system got to that state. For example, if you have a system consisting of 1 mol of He at 298 K and 1 atm, the system will have a given pressure, internal energy, entropy and free energy regardless of its history. You may have compressed the system from 2 atm, or heated the gas from 273 K. All this is irrelevant to specify the pressure, entropy, etc, because all these variables are what we call **state functions**. State functions depend only on the state of the system.

Other quantities such as work (w) and heat (q), on the other hand, are not state functions. There is no such a thing as an amount of work or heat in a system. The amounts of heat and work that "flow" during a process connecting specified initial and final states depend on how the process is carried out. Quantities that depend on the path followed between states are called **path functions**.

How is all this connected to differentials? Quantities whose values are independent of path are called state functions, and their differentials are exact (dP, dV, dG,dT...). Quantities that depend on the path followed between states are called path functions, and their differentials are inexact (dw, dq). As we will discuss in a moment, when we integrate an exact differential the result depends only on the final and initial points, but not on the path chosen. However, when we integrate an inexact differential, the path will have a huge influence in the result, even if we start and end at the same points. We'll come back to this shortly.

Knowing that a differential is exact will help you derive equations and prove relationships when you study thermodynamics in your advanced physical chemistry courses. For example, you will learn that all the state functions we mentioned above are related through these equations:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Here, we introduced two new state functions we haven't talked about yet: the enthalpy (H), and the Helmholtz free energy (A). You will learn about what they mean physically in CHM 346, but for now, just accept the fact that they are state functions, just as the entropy and the free energy. Although we didn't write it explicitly, T, P, V and S are not constants. When we talked about gases, we learned that P, V and T are not independent functions. If you change two of these variables you change the third, or in other words, you cannot independently vary the pressure, volume and temperature. The equation of state tells you how the three variables depend on each other. For one mole of gas, you can write the equation of state as a function $P = P(V, T)$, or as a function $V = V(T, P)$, or as a function $T = T(P, V)$. In the same way, you cannot independently change the pressure, volume, temperature and entropy of a system. If you modify the pressure and temperature, the volume and entropy will change as well. To make this clear, we can re-write the equations above as:

$$dU = T(S, V)dS - P(S, V)dV \tag{9.3.1}$$

$$dH = T(S, P)dS + V(S, P)dP \tag{9.3.2}$$

$$dA = -S(T, V)dT - P(T, V)dV \tag{9.3.3}$$

$$dG = -S(T, P)dT + V(T, P)dP \tag{9.3.4}$$

Because U, H, A and G are all state functions, their differentials are exact. We can derive a few relationships just from this fact.

For example, we see that $G = G(T, P)$, and because it's total differential, by definition, is:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \tag{9.3.5}$$

from Equations 9.3.4 and 9.3.5, we rapidly conclude that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

With minimal math, we concluded that if we change the pressure of a system at constant temperature, the rate of change of the free energy equals the volume. At this point this does not mean a lot to you, but hopefully you can appreciate how knowing that G is a state function is enough for you to derive a thermodynamic relationship! We can take this even further. Because G is a state function, dG is exact, and therefore, from Equation 9.3.4:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{9.3.6}$$

We just derived one of the four Maxwell relations. You can derive the other three from Equations 9.3.1-9.3.3. Notice that once again, we derived this equation from the knowledge that G is a state function. Why are these equations useful? Let's see an example using Equation 9.3.6. We can integrate this expression with T constant to get:

$$\int_{P_1}^{P_2} dS = \Delta S = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP \;(\text{constant T})$$

This equation tells you that the change in entropy in a system can be calculated by integrating $\left(\frac{\partial V}{\partial T}\right)_P$ data. This is extremely powerful, as we can easily measure temperature, pressure and volume in the lab, but we don't have an instrument that directly measures entropy!

9.4: A Mathematical Toolbox

In Chapter 8 we learned some important properties of partial derivatives, and in this chapter we learned about exact and inexact differentials. We saw many examples where these properties can be used to create relationships between thermodynamic variables. Usually we will try to calculate what we want from information we have (which is usually the information we can access experimentally). We just saw how we can calculate a change in entropy from quantities that are easy to measure in the lab: volume, temperature and pressure. In Chapter 8 we saw how we can get an expression of a partial derivative from partial derivatives that are much easier to calculate.

I will summarize some of these mathematical relationships, and call it our “toolbox”. The more comfortable you get using these relationships, the easier it will be for you to derive the thermodynamic relationships you will come across in your advanced physical chemistry courses.

1. The Euler reciprocity rule (Equation $8.1.1$): $\left(\frac{\partial^2 f}{\partial x \partial y}\right)=\left(\frac{\partial^2 f}{\partial y \partial x}\right)$
2. The inverse rule (Equation $8.1.2$): $\left(\frac{\partial y}{\partial x}\right)=\frac{1}{\left(\frac{\partial x}{\partial y}\right)}$
3. The cycle rule (Equation $8.1.3$) $\left(\frac{\partial y}{\partial x}\right)_z\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x=-1$
4. The chain rule (Equations $8.3.4$ and $8.3.5$):
   $\left(\frac{\partial u}{\partial r}\right)_\theta=\left(\frac{\partial u}{\partial x}\right)_y\left(\frac{\partial x}{\partial r}\right)_\theta+\left(\frac{\partial u}{\partial y}\right)_x\left(\frac{\partial y}{\partial r}\right)_\theta$
   $\left(\frac{\partial u}{\partial \theta}\right)_r=\left(\frac{\partial u}{\partial x}\right)_y\left(\frac{\partial x}{\partial \theta}\right)_r+\left(\frac{\partial u}{\partial y}\right)_x\left(\frac{\partial y}{\partial \theta}\right)_r$
5. The definition of the total differential (Equation $9.1.7$): $du=\left(\frac{\partial u}{\partial x_1}\right)_{x_2 \ldots x_n} dx_1+\left(\frac{\partial u}{\partial x_2}\right)_{x_1, x_3 \ldots x_n} dx_2+\ldots+\left(\frac{\partial u}{\partial x_n}\right)_{x_1 \ldots x_{n-1}} dx_n$
6. The concept of exact differential (Section 9.2)

9.5: Line Integrals

In Section 9.1, we discussed that in order to properly calculate the change in pressure we would need to integrate the differential defined in Equation 9.5.1:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \tag{9.5.1}$$

This raises the question of how to integrate differentials such as this one. Before we focus on this question, let's discuss what we expect for an exact differential. Let's say that we know how to perform these integrals, and we integrate dP from initial pressure (P_i) to final pressure (P_f) to calculate ΔP for a change that is not infinitesimal:

$$\Delta P = \int_{P_i}^{P_f} dP$$

Would it surprise you that the result equals the final pressure minus the initial pressure?

$$\Delta P = P_f - P_i$$

Hopefully not; the change in pressure will obviously be the final pressure minus the initial pressure, regardless of whether we did this slowly, fast, at constant volume, constant temperature, etc. In other words, you just need the information of the state of the system at the beginning and the end of the process, but you do not need to know anything about what happened in between. All this makes sense because P is a state function, and the same argument applies to other state functions, such as entropy, internal energy, free energy, etc. We just reached an important conclusion: if we integrate an exact differential, the result will be independent of the path, and it will equal the function at the end point minus the function at the initial point. If we integrate an inexact differential this is not true, because we will be integrating the differential of a function that is *not* a state function. We'll come back to this many times, but it is important that before getting lost in the math we keep in mind what to expect.

We already mentioned the word "path", but what do we mean by that? In the example of the gas, the path would be described by the values of the temperature and volume at all times. For example, Figure 9.5.1 shows two possible paths that result in the same change in pressure. We could imagine an infinite number of other options, and of course we are not restricted to keeping one variable constant while changing the other.

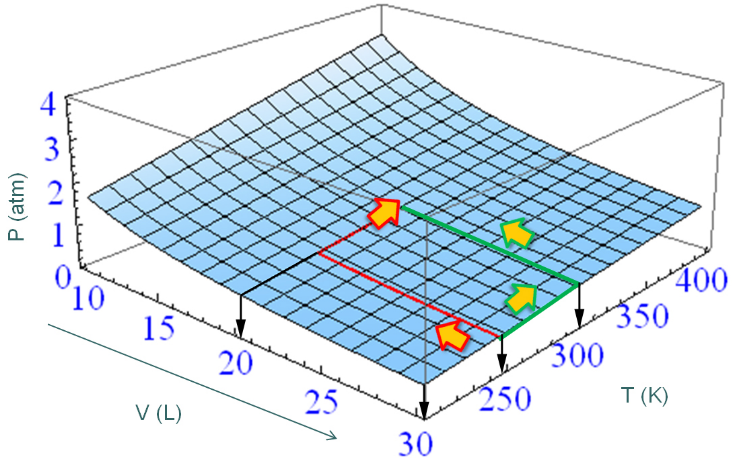


Figure 9.5.1: Two different paths that produce the same change in pressure in one mole of an ideal gas. In the first case (red), the volume is compressed from 30 L to 20 L at 250 K, and then the temperature is increased to 300 K at constant pressure. In the second case (green) the temperature is first raised to 300 K at a constant volume of 30L, and then the system is compressed to 20L at constant temperature The blue surface represents the function $P = RT/V$ (CC BY-NC-SA; Marcia Levitus)

We can integrate dP along one path or the other, but we already know what we will get: $\int dP = P_2 - P_1$ regardless of the path. Work and heat, on the other hand, are not state functions. There is no such a thing as an amount of work or heat in a system. The amounts of heat and work that "flow" during a process connecting specified initial and final states depend on how the process is carried out. This means that if we want to calculate the work or the heat involved in the process, we would need to integrate the inexact differentials dw and dq indicating the particular path used to take the system from the initial to the final states:

$$q = \int\limits_{path} dq$$

$$w = \int\limits_{path} dw$$

For one mole of an ideal gas ($P = RT/V$),

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT = -\frac{RT}{V^2}dV + \frac{R}{V}dT$$

From our previous discussion, we know the result of integrating the differential

$$dP = -\frac{RT}{V^2}dV + \frac{R}{V}dT$$

along any path. The result should be the final pressure minus the initial pressure:

$$\Delta P = R(T_f/V_f - T_i/V_i) \tag{9.5.2}$$

where the subscripts f and i refer to the final and initial states.

Even is we know the answer, let's do it anyway so we learn how to integrate differentials. We will consider the two paths depicted in Figure $9.5.1$. In both cases the initial temperature is 250 K, the initial volume is 30 L, the final temperature is 300 K, and the final volume is 20 L.

Let's start with the 'red' path. This path is the sum of two components, one where we change the volume at constant temperature, and another one where we change the temperature at constant volume. Let's call these individual steps path 1 and path 2, so the total path is path1 + path 2:

$$\int\limits_{path} dP = \int\limits_{path1} dP + \int\limits_{path2} dP$$

$$\int\limits_{path} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right) = \int\limits_{path1} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right) + \int\limits_{path2} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right)$$

In path 1, we keep the temperature constant, so $dT = 0$. Furthermore, the temperature equals T_i during the whole process:

$$\int\limits_{path1} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right) = \int\limits_{path1} \left(-\frac{RT_i}{V^2}dV\right) = \int_{V_i}^{V_f} -\frac{RT_i}{V^2}dV$$

in path 2 we keep the volume constant, so $dV = 0$. Furthermore, the volume equals V_f during the whole process:

$$\int\limits_{path2} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right) = \int\limits_{path2} \frac{R}{V_f}dT = \int_{T_i}^{T_f} \frac{R}{V_f}dT$$

Putting the two results together:

$$\int\limits_{path} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right) = \int_{V_i}^{V_f} -\frac{RT_i}{V^2}dV + \int_{T_i}^{T_f} \frac{R}{V_f}dT$$

$$\int\limits_{path} \left(-\frac{RT}{V^2}dV + \frac{R}{V}dT\right) = \frac{RT_i}{V}\bigg|_{V_i}^{V_f} + \frac{RT}{V_f}\bigg|_{T_i}^{T_f} = RT_i\left(\frac{1}{V_f} - \frac{1}{V_i}\right) + \frac{R}{V_f}(T_f - T_i)$$

$$RT_i\left(\frac{1}{V_f} - \frac{1}{V_i}\right) + \frac{R}{V_f}(T_f - T_i) = R\left(\frac{T_i}{V_f} - \frac{T_i}{V_i} + \frac{T_f}{V_f} - \frac{T_i}{V_f}\right) = R\left(\frac{T_f}{V_f} - \frac{T_i}{V_i}\right)$$

The result is, as expected, identical to Equation 9.5.2.

Let's now consider the two-step path depicted in green in Figure $9.5.1$. We'll follow the same ideas we used for the path shown in red. In the first part of the path we change the temperature from T_i to T_f at constant volume, $V=V_i$. In the second part of the path we change the volume from V_i to V_f at constant temperature, $T=T_f$. In the first part, $dV=0$ and $V=V_i$ at all times. In the second part, $dT=0$, and $T=T_f$ at all times:

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=\int_{T_i}^{T_f}\left(\frac{R}{V_i}dT\right)+\int_{V_i}^{V_f}\left(-\frac{RT_f}{V^2}dV\right)$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=\frac{RT}{V_i}\bigg|_{T_i}^{T_f}+\frac{RT_f}{V}\bigg|_{V_i}^{V_f}$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=\frac{R}{V_i}(T_f-T_i)+RT_f\left(\frac{1}{V_f}-\frac{1}{V_i}\right)=R\left(\frac{T_f}{V_f}-\frac{T_i}{V_i}\right)$$

The result is, as expected, P_f-P_i (Equation $9.5.2$).

Because dP is exact, it does not matter which path we choose to go from (V_i,P_i) to (V_f,P_f), the result of the integral of dP will always the same $R\left(\frac{T_f}{V_f}-\frac{T_i}{V_i}\right)$. Let's try another path; this time one that does not keep any of the variables constant at any time. Consider the path that is the straight line that joins the points (V_i,P_i) to (V_f,P_f). In order to integrate dP along a particular path, we need the equation of the path indicating how the variables V and T are connected at all times.

In this case, $T=a+bV$, where a is the $y-$intercept and b is the slope. You should be able to prove that the values of a and b for this path are:

$$a=T_i-\frac{T_f-T_i}{V_f-V_i}V_i$$

$$b=\frac{T_f-T_i}{V_f-V_i}$$

Because $T=a+bV$, $dT=bdV$, $V=(T-a)/b$, and $dV=dT/b$. These relationships tell us how T and V are connected throughout the path, and we can therefore write these equivalent expressions:

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=-\int_{V_i}^{V_f}\left(-\frac{R(a+bV)}{V^2}dV\right)+\int_{T_i}^{T_f}\left(\frac{bR}{T-a}dT\right)$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=-\int_{V_i}^{V_f}\left(-\frac{R(a+bV)}{V^2}dV\right)+\int_{V_i}^{V_f}\left(\frac{R}{V}bdV\right)$$

$$\int_{path}\left(-\frac{RT}{V^2}dV+\frac{R}{V}dT\right)=-\int_{T_i}^{T_f}\left(-\frac{RT}{[(T-a)/b]^2}\frac{1}{b}dT\right)+\int_{T_i}^{T_f}\left(\frac{bR}{T-a}\right)dT$$

In the first case we just wrote the first integrand in terms of V only and the second integrand in terms of T only. To achieve this, we used the information from the path to see how V and T are related as we move from our initial to our final states. The same idea applies to the second and third lines, where we wrote everything in terms of V or in terms of T. The three equations will give the same result regardless of whether the differential is exact on inexact. However, because we are integrating an exact differential, the result will be identical to the result we got for the two other paths that share the same initial and final state, and also identical to P_f-P_i.

The three equations above are not too hard to solve, but they are more time consuming that the integrals we had to solve for the paths involving sections of the path where one or the other variable remain constant. This is powerful, because it means that if you are integrating an exact differential, you can get smart and solve the integral for a very easy path, as long as the initial and final states are the same. You know the result will be the same because the differential is exact. If, on the other hand, the differential is inexact, we are out of luck. The integral depends on the path, so we need to solve the path we are given.

Because dP is exact, the line integral equals $P_f - P_i$. A consequence of this is that the integral along a closed path (one where $P_i = P_f$) is zero. Mathematically:

$$\oint dP = 0$$

where the circle inside the integration symbol means that the path is closed. This is true for any exact differential, but not necessarily true for a differential that is inexact. Coming back to thermodynamics, imagine one mole of a gas in a container whose volume is first reduced from 30 L to 20 L at a constant temperature T= 250 K. You then heat the gas up to 300 K keeping the volume constant, then increase the volume back to 30 L keeping the temperature constant, and finally cool it down to 250 K at constant volume (see Figure $9.5.1$. Because the initial and final states are the same, the line integral of any state function is zero:

$$\Delta P = \oint dP = 0$$

$$\Delta G = \oint dG = 0$$

$$\Delta S = \oint dS = 0$$

etc, etc

This closed path does not involve a change in pressure, free energy or entropy, because these functions are state functions, and the final state is identical to the initial state.

On the other hand,

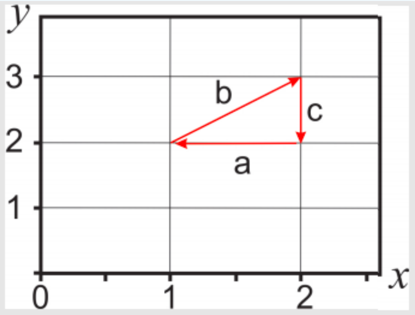
$$w = \oint dw \neq 0$$

$$q = \oint dq \neq 0$$

because we are integrating inexact differentials. Physically, you had to do work to expand the gas, heat it up, compress it, cool it down, etc. It does not matter you end up exactly where you started, work and heat were involved in the process. It may be possible for a particular closed path to yield $w = 0$ or $q = 0$, but in general this does not need to be the case.

✓ Example $9.5.1$

Given the following differential $dz = x\ dy + 2y\ dx$, and the closed path shown in the figure, calculate the line integral $\int_{path} dz$



Note: This problem is also available in video format: http://tinyurl.com/mszuwr7

Solution

The path is divided in three sections, so

$$\int_{path} dz = \int_a dz + \int_b dz + \int_c dz$$

In section a: $y = 2$, $dy = 0$ (y is a constant), and x changes from an initial value of 2 to a final value of 1:

$$\int_a dz = \int_2^1 4dx = 4x|_2^1 = 4 - 8 = -4$$

In section b: $y = 1 + x$, $dy = dx$, and x changes from an initial value of 1 to a final value of 2:

$$\int_b dz = \int_b x\ dy + 2y\ dx = \int_1^2 x\ dx + \int_1^2 2(1+x)\ dx = \frac{x^2}{2}\bigg|_1^2 + 2\frac{(1+x)^2}{2}\bigg|_1^2 = \frac{3}{2} + (9-4) = \frac{13}{2}$$

In section c: $x = 2$, $dx = 0$ (x is a constant), and y changes from an initial value of 3 to a final value of 2:

$$\int_c dz = \int_3^2 2dy = 2y|_3^2 = 4 - 6 = -2$$

Therefore,

$$\int\limits_{path} dz = \int_a dz + \int_b dz + \int_c dz = -4 + 13/2 - 2 = 1/2$$

Notice that the integral is not zero even if the path was closed. This is not surprising given that the differential was inexact.

✓ Example 9.5.2

Consider the differential

$$du = (x^2 - y^2)dx + (2xy)dy$$

a. Is du exact or inexact?
b. Explain why each of the following is true or false:
   - du is the total differential of some function $u(x,y)$. Find $u(x,y)$ if possible.
   - $\int_a du = \int_b du = \int_c du$ as long as a, b and c are paths in the (x,y) space that share the same starting and ending points.

c. Calculate $\int\limits_{path} du$ if the path is the straight line joining the points (0,2) and (2,0).

Solution:

To test whether du is exact or inexact, we compare the following derivatives

$$\left(\frac{\partial(x^2 - y^2)}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial(2xy)}{\partial x}\right)_y$$

Because the two partial derivatives are not the same, the differential is inexact.

Because the differential is inexact, it is not the total differential of a function $u(x,y)$. We cannot find the function because it does not exist.

The line integrals $\int_a du$, $\int_b du$ and $\int_c du$ will in principle be different because the integral of an inexact differential depends not only on the initial and final states, but also on the path used to get from the initial to the final state. The statement would be true for an exact differential.

To calculate the integral along the straight line joining the points (0,2) and (2,0), we first need to find the equation $y(x)$ that describes this path. Sketching the function is not a must, but it might help:

The equation of this straight line is $y = 2 - x$. Therefore, along the path, $y = 2 - x$ and $dy = -dx$. The variable x changes from an initial value $x = 0$ to a final value $x = 2$:

$$\int_{path} du = \int_{path} (x^2 - y^2)dx + (2xy)dy$$

It is important to stress that x and y are not independent along the process, but instead, they are connected through the equation of the path. We will write the equation in terms of x (we could do it in terms of y with identical results):

$$\begin{aligned}
\int_{path} du &= \int_{path} (x^2 - y^2)dx + (2xy)dy \\
&= \int_0^2 (x^2 - (2-x)^2)dx + \int_0^2 (2x(2-x))(-dx) \\
&= \int_0^2 (x^2 - (4 + x^2 - 4x))dx - \int_0^2 (4x - 2x^2)dx \\
&= \int_0^2 (4x - 4)dx - \int_0^2 (4x - 2x^2)dx = \int_0^2 (2x^2 - 4)dx \\
&= \left(\frac{2x^3}{3} - 4x\right)\Bigg|_0^2 = \frac{16}{3} - 8 = -\frac{8}{3} \\
&= -\frac{8}{3}
\end{aligned}$$

9.6: Exact and Inexact Differentials (Summary)

To summarize, given a function $f(x,y)$, its total differential df is, by definition:

$$df=\left(\frac{\partial f}{\partial x}\right)_y dx+\left(\frac{\partial f}{\partial y}\right)_x dy$$

Given an arbitrary differential

$$df=M(x,y)dx+N(x,y)dy$$

where M and N are functions of x and y, the differential is **exact** if it is the total differential of a function $f(x,y)$. To test for exactness we compare the partial derivative of $M(x,y)$ with respect to y, and the partial derivative of $N(x,y)$ with respect to x:

$$\left(\frac{\partial M(x,y)}{\partial y}\right)_x \overset{?}{=} \left(\frac{\partial N(x,y)}{\partial x}\right)_y$$

If the derivatives are identical, we conclude that the differential df is exact, and therefore it is the total differential of a function $f(x,y)$. To find the function, we notice that for an exact differential:

$$M(x,y)=\left(\frac{\partial f}{\partial x}\right)_y$$

$$N(x,y)=\left(\frac{\partial f}{\partial y}\right)_x$$

We can then find the function by partial integration:

$$f(x,y)=\int df=\int M(x,y)dx \text{ (at constant } y)$$

$$f(x,y)=\int df=\int N(x,y)dy \text{ (at constant } x)$$

It is important to keep in mind that the integration constant in the first case will be an arbitrary function of y, and in the second case an arbitrary function of x.

For an exact differential, the line integral does not depend on the path, but only on the initial and final points. Furthermore, because the differential is exact, it is the total differential of a state function $f(x,y)$. This means that the integral of df along any path is simply the function f evaluated at the final state minus the function f evaluated at the initial state:

$$\int_c M(x,y)dx+N(x,y)dy=\int_c df=\Delta f=f(x_2,y_2)-f(x_1,y_1)$$

where c represents the path that starts at the point (x_1,y_1) and ends at the point (x_2,y_2).

If the initial and the final states are identical, for an exact differential:

$$\oint df=0$$

For an inexact differential, $\int_c df$ will in general depend on the path c.

9.7: Problems

Problem 9.7.1

Determine whether the following differentials are exact or inexact. If they are exact, determine $u = u(x, y)$.

1. $du = (2ax + by)dx + (bx + 2cy)dy$
2. $du = (x^2 - y^2)dx + (2xy)dy$

Problem 9.7.2

Determine whether dz is exact or inexact. If it is exact, determine $z = z(P, T)$.

$$dz = -\frac{RT}{P^2}dP + \frac{R}{P}dT$$

Problem 9.7.3

From Equation 9.7.4, and using the fact that G is a state function, prove that the change in entropy (ΔS) of one mole of an ideal gas whose pressure changes from an initial value P_1 to a final value P_2 at constant temperature is:

$$\Delta S = -R\ln\frac{P_2}{P_1}$$

Problem 9.7.4

From Equations 9.7.1-9.7.3, and using the fact that U, H and A are state functions, derive the three corresponding Maxwell relations.

Answer

Add texts here. Do not delete this text first.

Problem 9.7.5

Given the following differential:

$$dz = xydx + 2ydy$$

a. Determine if it is exact or inexact. If it is, obtain $z(x, y)$
b. Calculate the line integrals $\int_c dz$ for the paths enumerated below:
   1. the line $y = 2x$ from $x = 0$ to $x = 2$
   2. the curve $y = x^2$ from $x = 0$ to $x = 2$
   3. any other path of your choice that joins the same initial and final points.

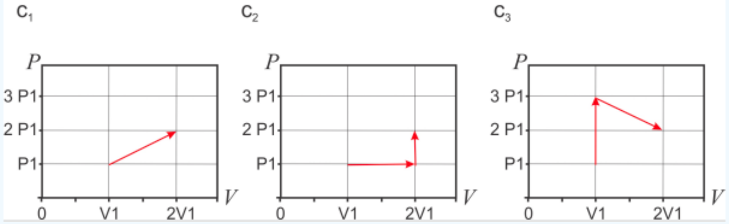
Problem 9.7.6

For a mole of a perfect monoatomic gas, the internal energy can be expressed as a function of the pressure and volume as

$$U = \frac{3}{2}PV$$

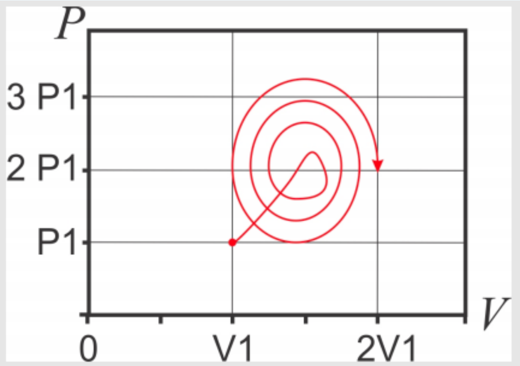
a. Write the total differential of U, dU.

b. Calculate the line integrals $\int_c dU$ for the paths shown below (c_1, c_2, c_3):



c. Calculate $U(V_f, P_f) - U(V_i, P_i)$ and compare with the results of b) (Note: f refers to the final state and i to the initial state).

d. Considering your previous results, calculate $\int_c dU$ for the path below:



As defined in Section 9.3,

$$dU = T(S,V)dS - P(S,V)dV \tag{9.7.1}$$

$$dH = T(S,P)dS + V(S,P)dP \tag{9.7.2}$$

$$dA = -S(T,V)dT - P(T,V)dV \tag{9.7.3}$$

$$dG = -S(T,P)dT + V(T,P)dP \tag{9.7.4}$$

CHAPTER OVERVIEW

10: Plane Polar and Spherical Coordinates

Objectives

- Understand the concept of area and volume elements in cartesian, polar and spherical coordinates.
- Be able to integrate functions expressed in polar or spherical coordinates.
- Understand how to normalize orbitals expressed in spherical coordinates, and perform calculations involving triple integrals.
- Understand the concept of probability distribution function.

10.1: Coordinate Systems

The simplest coordinate system consists of coordinate axes oriented perpendicularly to each other. These coordinates are known as cartesian coordinates or rectangular coordinates, and you are already familiar with their two-dimensional and three-dimensional representation. In the plane, any point P can be represented by two signed numbers, usually written as (x, y), where the coordinate x is the distance perpendicular to the x axis, and the coordinate y is the distance perpendicular to the y axis (Figure $10.1.1$, left). In space, a point is represented by three signed numbers, usually written as (x, y, z) (Figure $10.1.1$, right).

Often, positions are represented by a vector, $\vec{r}$, shown in red in Figure $10.1.1$. In three dimensions, this vector can be expressed in terms of the coordinate values as $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$, where $\hat{i} = (1, 0, 0)$, $\hat{j} = (0, 1, 0)$ and $\hat{z} = (0, 0, 1)$ are the so-called unit vectors.

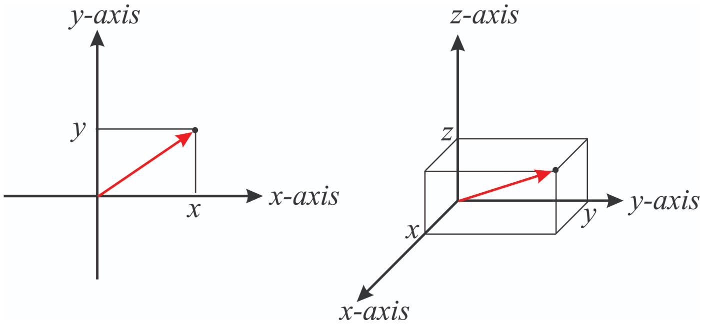


Figure 10.1.1: Cartesian coordinates (CC BY-NC-SA; Marcia Levitus)

We already know that often the symmetry of a problem makes it natural (and easier!) to use other coordinate systems. In two dimensions, the polar coordinate system defines a point in the plane by two numbers: the distance r to the origin, and the angle θ that the position vector forms with the x-axis. Notice the difference between $\vec{r}$, a vector, and r, the distance to the origin (and therefore the modulus of the vector). Vectors are often denoted in bold face (e.g. **r**) without the arrow on top, so be careful not to confuse it with r, which is a scalar.

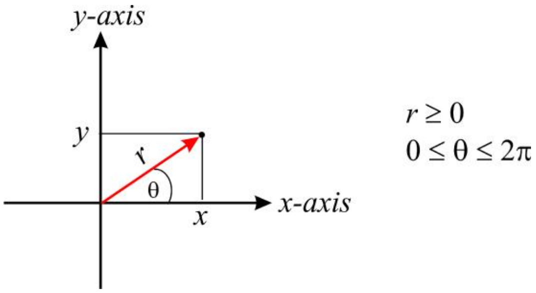


Figure 10.1.2: Plane polar coordinates (CC BY-NC-SA; Marcia Levitus)

While in cartesian coordinates x, y (and z in three-dimensions) can take values from $-\infty$ to ∞, in polar coordinates r is a positive value (consistent with a distance), and θ can take values in the range $[0, 2\pi]$.

The relationship between the cartesian and polar coordinates in two dimensions can be summarized as:

$$x = r\cos\theta \tag{10.1.1}$$

$$y = r\sin\theta \tag{10.1.2}$$

$$r^2 = x^2 + y^2 \tag{10.1.3}$$

$$\tan\theta = y/x \tag{10.1.4}$$

In three dimensions, the spherical coordinate system defines a point in space by three numbers: the distance r to the origin, a polar angle ϕ that measures the angle between the positive x-axis and the line from the origin to the point P projected onto the xy-plane, and the angle θ defined as the is the angle between the z-axis and the line from the origin to the point P:

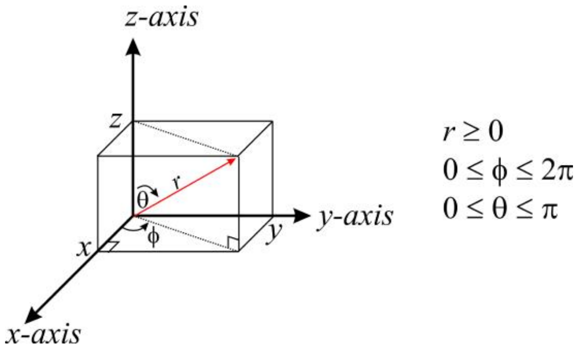


Figure 10.1.3: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

Before we move on, it is important to mention that depending on the field, you may see the Greek letter θ (instead of ϕ) used for the angle between the positive x-axis and the line from the origin to the point P projected onto the xy-plane. That is, θ and ϕ may appear interchanged. This can be very confusing, so you will have to be careful. When using spherical coordinates, it is important that you see how these two angles are defined so you can identify which is which.

Spherical coordinates are useful in analyzing systems that are symmetrical about a point. For example a sphere that has the cartesian equation $x^2+y^2+z^2=R^2$ has the very simple equation $r=R$ in spherical coordinates. Spherical coordinates are the natural coordinates for physical situations where there is spherical symmetry (e.g. atoms). The relationship between the cartesian coordinates and the spherical coordinates can be summarized as:

$$x = r\sin\theta\cos\phi \tag{10.1.5}$$

$$y = r\sin\theta\sin\phi \tag{10.1.6}$$

$$z = r\cos\theta \tag{10.1.7}$$

These relationships are not hard to derive if one considers the triangles shown in Figure 10.1.4:

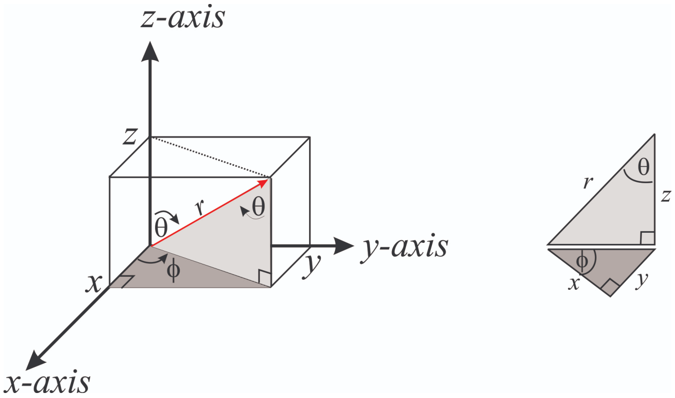


Figure 10.1.4: Spherical coordinates (CC BY-NC-SA; Marcia Levitus)

10.2: Area and Volume Elements

In any coordinate system it is useful to define a differential area and a differential volume element. In cartesian coordinates the differential area element is simply $dA = dx\ dy$ (Figure $10.2.1$), and the volume element is simply $dV = dx\ dy\ dz$.

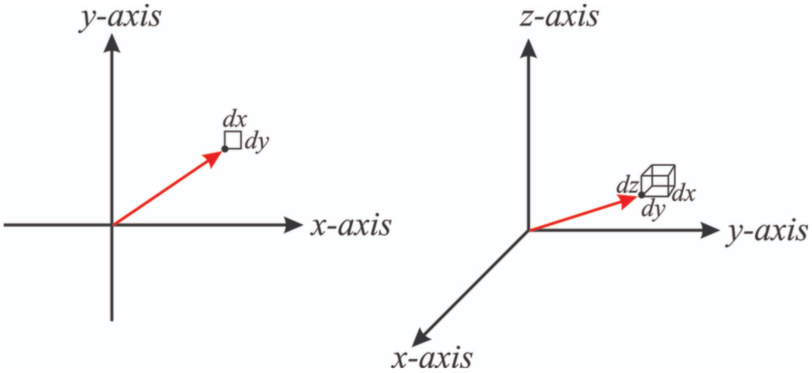


Figure $10.2.1$: Area and volume elements in cartesian coordinates (CC BY-NC-SA; Marcia Levitus)

We already performed double and triple integrals in cartesian coordinates, and used the area and volume elements without paying any special attention. For example, in example [c2v:c2vex1], we were required to integrate the function $|\psi(x,y,z)|^2$ over all space, and without thinking too much we used the volume element $dx\ dy\ dz$ (see page). We also knew that "all space" meant $-\infty \leq x \leq \infty$, $-\infty \leq y \leq \infty$ and $-\infty \leq z \leq \infty$, and therefore we wrote:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z)|^2\ dx\ dy\ dz = 1$$

But what if we had to integrate a function that is expressed in spherical coordinates? Would we just replace $dx\ dy\ dz$ by $dr\ d\theta\ d\phi$? The answer is no, because the volume element in spherical coordinates depends also on the actual position of the point. This will make more sense in a minute. Coming back to coordinates in two dimensions, it is intuitive to understand why the area element in cartesian coordinates is $dA = dx\ dy$ independently of the values of x and y. This is shown in the left side of Figure $10.2.2$ However, in polar coordinates, we see that the areas of the gray sections, which are both constructed by increasing r by dr, and by increasing θ by $d\theta$, depend on the actual value of r. Notice that the area highlighted in gray increases as we move away from the origin.

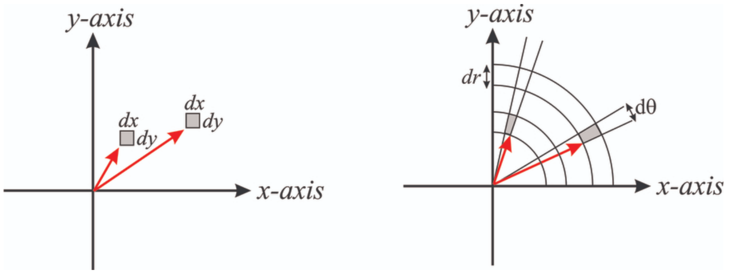


Figure $10.2.2$: Differential of area in cartesian and polar coordinates (CC BY-NC-SA; Marcia Levitus)

The area shown in gray can be calculated from geometrical arguments as

$$dA = \left[\pi(r+dr)^2 - \pi r^2\right]\frac{d\theta}{2\pi}.$$

Because $dr << 0$, we can neglect the term $(dr)^2$, and $dA = r\ dr\ d\theta$ (see Figure $10.2.3$).

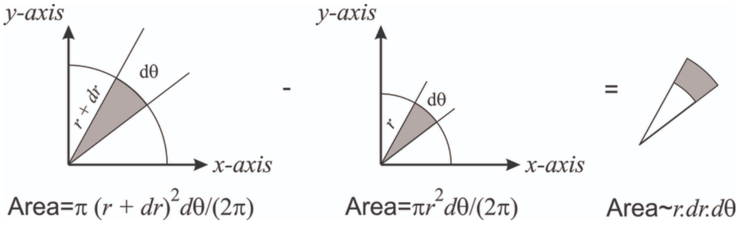


Figure $10.2.3$: Differential of area in polar coordinates (CC BY-NC-SA; Marcia Levitus)

Let's see how this affects a double integral with an example from quantum mechanics. The wave function of the ground state of a two dimensional harmonic oscillator is: $\psi(x,y)=Ae^{-a(x^2+y^2)}$. We know that the quantity $|\psi|^2$ represents a probability density, and as such, needs to be normalized:

$$\int\limits_{all\ space} |\psi|^2\, dA = 1$$

This statement is true regardless of whether the function is expressed in polar or cartesian coordinates. However, the limits of integration, and the expression used for dA, will depend on the coordinate system used in the integration.

In cartesian coordinates, "all space" means $-\infty<x<\infty$ and $-\infty<y<\infty$. The differential of area is $dA=dxdy$:

$$\int\limits_{all\ space} |\psi|^2\, dA = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} A^2 e^{-2a(x^2+y^2)}\, dxdy = 1$$

In polar coordinates, "all space" means $0<r<\infty$ and $0<\theta<2\pi$. The differential of area is $dA=r\, drd\theta$. The function $\psi(x,y)=Ae^{-a(x^2+y^2)}$ can be expressed in polar coordinates as: $\psi(r,\theta)=Ae^{-ar^2}$

$$\int\limits_{all\ space} |\psi|^2\, dA = \int\limits_{0}^{\infty}\int\limits_{0}^{2\pi} A^2 e^{-2ar^2} r\, d\theta dr = 1$$

Both versions of the double integral are equivalent, and both can be solved to find the value of the normalization constant (A) that makes the double integral equal to 1. In polar coordinates:

$$\int\limits_{0}^{\infty}\int\limits_{0}^{2\pi} A^2 e^{-2ar^2} r\, d\theta dr = A^2\int\limits_{0}^{\infty} e^{-2ar^2} r\, dr \int\limits_{0}^{2\pi} d\theta = A^2\times\frac{1}{4a}\times 2\pi = 1$$

Therefore[1], $A=\sqrt{2a/\pi}$. The same value is of course obtained by integrating in cartesian coordinates.

It is now time to turn our attention to triple integrals in spherical coordinates. In cartesian coordinates, the differential volume element is simply $dV=dx\,dy\,dz$, regardless of the values of x, y and z. Using the same arguments we used for polar coordinates in the plane, we will see that the differential of volume in spherical coordinates is not $dV=dr\,d\theta\,d\phi$. The geometrical derivation of the volume is a little bit more complicated, but from Figure $10.2.4$you should be able to see that dV depends on r and θ, but not on ϕ. The volume of the shaded region is

$$dV=r^2\sin\theta\, d\theta\, d\phi\, dr \tag{10.2.1}$$

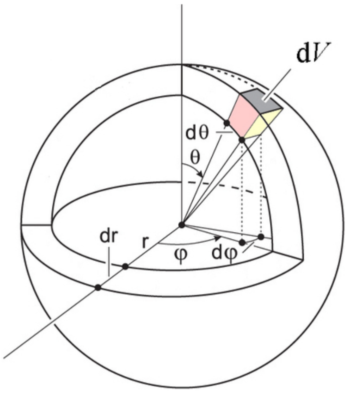


Figure 10.2.4: Differential of volume in spherical coordinates (CC BY-NC-SA; Marcia Levitus)

We will exemplify the use of triple integrals in spherical coordinates with some problems from quantum mechanics. We already introduced the Schrödinger equation, and even solved it for a simple system in Section 5.4. We also mentioned that spherical coordinates are the obvious choice when writing this and other equations for systems such as atoms, which are symmetric around a point.

As we saw in the case of the particle in the box (Section 5.4), the solution of the Schrödinger equation has an arbitrary multiplicative constant. Because of the probabilistic interpretation of wave functions, we determine this constant by normalization. The same situation arises in three dimensions when we solve the Schrödinger equation to obtain the expressions that describe the possible states of the electron in the hydrogen atom (i.e. the orbitals of the atom). The Schrödinger equation is a partial differential equation in three dimensions, and the solutions will be wave functions that are functions of r, θ and ϕ. The lowest energy state, which in chemistry we call the 1s orbital, turns out to be:

$$\psi_{1s} = Ae^{-r/a_0}$$

This particular orbital depends on r only, which should not surprise a chemist given that the electron density in all s-orbitals is spherically symmetric. We will see that p and d orbitals depend on the angles as well. Regardless of the orbital, and the coordinate system, the normalization condition states that:

$$\int\limits_{all\ space} |\psi|^2\, dV = 1$$

For a wave function expressed in cartesian coordinates,

$$\int\limits_{all\ space} |\psi|^2\, dV = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} \psi^*(x,y,z)\psi(x,y,z)\, dxdydz$$

where we used the fact that $|\psi|^2 = \psi^*\psi$.

In spherical coordinates, “all space” means $0 \leq r \leq \infty$, $0 \leq \phi \leq 2\pi$ and $0 \leq \theta \leq \pi$. The differential dV is $dV = r^2 \sin\theta\, d\theta\, d\phi\, dr$, so

$$\int\limits_{all\ space} |\psi|^2\, dV = \int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = 1$$

Let’s see how we can normalize orbitals using triple integrals in spherical coordinates.

✓ Example 10.2.1

When solving the Schrödinger equation for the hydrogen atom, we obtain $\psi_{1s} = Ae^{-r/a_0}$, where A is an arbitrary constant that needs to be determined by normalization. Find A.

Solution

In spherical coordinates,

$$\int\limits_{all\ space} |\psi|^2\, dV = \int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = 1$$

because this orbital is a real function, $\psi^*(r,\theta,\phi)\psi(r,\theta,\phi) = \psi^2(r,\theta,\phi)$. In this case, $\psi^2(r,\theta,\phi) = A^2 e^{-2r/a_0}$.

Therefore,

$$\int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{\infty} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\, r^2 \sin\theta\, drd\theta d\phi = \int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{\infty} A^2 e^{-2r/a_0}\, r^2 \sin\theta\, drd\theta d\phi = 1$$

$$\int\limits_{0}^{2\pi}\int\limits_{0}^{\pi}\int\limits_{0}^{\infty} A^2 e^{-2r/a_0}\, r^2 \sin\theta\, drd\theta d\phi = A^2 \int\limits_{0}^{2\pi} d\phi \int\limits_{0}^{\pi} \sin\theta\; d\theta \int\limits_{0}^{\infty} e^{-2r/a_0}\, r^2\; dr$$

The result is a product of three integrals in one variable:

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{\pi} \sin\theta \; d\theta = -\cos\theta|_0^{\pi} = 2$$

$$\int_0^{\infty} e^{-2r/a_0} \, r^2 \; dr = ?$$

From the formula sheet:

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}},$$

where $a > 0$ and n is a positive integer.

In this case, $n = 2$ and $a = 2/a_0$, so:

$$\int_0^{\infty} e^{-2r/a_0} \, r^2 \; dr = \frac{2!}{(2/a_0)^3} = \frac{2}{8/a_0^3} = \frac{a_0^3}{4}$$

Putting the three pieces together:

$$A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \; d\theta \int_0^{\infty} e^{-2r/a_0} \, r^2 \; dr = A^2 \times 2\pi \times 2 \times \frac{a_0^3}{4} = 1$$

$$A^2 \times \pi \times a_0^3 = 1 \rightarrow A = \frac{1}{\sqrt{\pi a_0^3}}$$

The normalized 1s orbital is, therefore:

$$\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

10.3: A Refresher on Electronic Quantum Numbers

Each electron in an atom is described by four different quantum numbers.

- Principal quantum number: $n=1,2,3 \ldots \infty$. It determines the overall size and energy of an orbital.
- Angular momentum quantum number: $l=0,1,2 \ldots(n-1)$. It is related with the shape of the orbital. In chemistry, we usually use the letters $s, p, d, f \ldots$ to denote an orbital with $l=0,1,2,3 \ldots$ For example, for the 1s orbital, $n=1$ and $l=0$.
- Magnetic quantum number: $m_l=-l,-l+1, \ldots, 0, \ldots l-1, l$. It specifies the orientation of the orbital. For a p orbital, for example, $l=1$ and therefore m_l can take the values $-1,0,1$. In general, there are $2l+1$ values of m_l for a given value of l. That is why p orbitals come in groups of 3, d orbitals come in groups of 5, etc.
- Spin quantum number: $m_s=-1/2$ or $1/2$. The Pauli exclusion principle states that no two electrons in the same atom can have identical values for all four of their quantum numbers. This means that no more than two electrons can occupy the same orbital, and that two electrons in the same orbital must have opposite spins.

The first three quantum numbers specify the particular orbital the electron occupies. For example, the orbital $2p_{-1}$ is the orbital with $n=2$, $l=1$ and $m_l=-1$. Two electrons of opposite spin can occupy this orbital.

So far we've been limited to the 1s orbital, but now that we are more comfortable with the nomenclature of orbitals, we can start doing some math with orbitals that have more complex expressions.

Example 10.3.1:

After solving the Schrödinger equation for the hydrogen atom, we obtain the following expression for the $2p_{+1}$ orbital:

$$\psi_{2p_{+1}}=Are^{-r/(2a_0)}\sin\theta e^{i\phi}$$

as usual, we obtain the constant A from the normalization condition. Calculate A.

Solution

In three dimensions, the normalization condition is:

$$\int\limits_{all\ space}|\psi|^2\,dV=1$$

Because the orbital is expressed in spherical coordinates:

$$\int\limits_{all\ space}|\psi|^2\,dV=\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\,r^2\sin\theta\,drd\theta d\phi=1$$

For this particular orbital:

$$\psi_{2p_{+1}}=Are^{-r/(2a_0)}\sin\theta e^{i\phi}$$

$$\psi^*_{2p_{+1}}=Are^{-r/(2a_0)}\sin\theta e^{-i\phi}$$

$$\psi^*_{2p_{+1}}\psi_{2p_{+1}}=A^2r^2e^{-r/(a_0)}\sin^2\theta\left(e^{i\phi}e^{-i\phi}\right)=A^2r^2e^{-r/(a_0)}\sin^2\theta$$

so,

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi^*(r,\theta,\phi)\psi(r,\theta,\phi)\,r^2\sin\theta\,drd\theta d\phi=\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}{\color{red}A^2r^2e^{-r/(a_0)}\sin^2\theta}\,{\color{blue}r^2\sin\theta\,drd\theta d\phi}=1$$

where the part of the integrand highlighted in blue comes from the differential of volume (dV) and the part in red comes from $|\psi|^2$. We need to integrate the whole expression, so:

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} A^2 r^2 e^{-r/(a_0)} \sin^2\theta\, r^2 \sin\theta\, dr d\theta d\phi = A^2 \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^4 e^{-r/(a_0)} \sin^3\theta\, dr d\theta d\phi = A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} r^4 e^{-r/(a_0)}\, dr$$

$$\int_0^{2\pi} d\phi = 2\pi$$

$$\int_0^{\pi} \sin^3\theta\, d\theta = ?$$

From the formula sheet: $\int sin^3(ax)\,dx = \frac{1}{12a}\cos(3ax) - \frac{3}{4a}\cos(ax) + C$ so,

$$\int_0^{\pi} sin^3\theta\, d\theta = \frac{1}{12}\cos(3\pi) - \frac{3}{4}\cos(\pi) - \frac{1}{12}\cos(0) + \frac{3}{4}\cos(0) = \frac{1}{12}(-1) - \frac{3}{4}(-1) - \frac{1}{12}(1) + \frac{3}{4}(1) = \frac{4}{3}$$

$$\int_0^{\infty} r^4 e^{-r/(a_0)}\, dr = ?$$

From the formula sheet:

$\int_0^{\infty} x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}},\ a > 0, n$ is a positive integer.

Here, $a = 1/a_o$ and $n = 4$, so:

$$\int_0^{\infty} r^4 e^{-r/(a_0)}\, dr = \frac{4!}{(1/a_0)^5} = 24a_0^5$$

Putting the three pieces together:

$$A^2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{\infty} r^4 e^{-r/(a_0)}\, dr = A^2 \times 2\pi \times \frac{4}{3} \times 24a_0^5 = 64a_0^5\pi A^2 = 1$$

Solving for A:

$$A = \frac{1}{8\left(a_0^5\pi\right)^{1/2}}$$

The normalized orbital is, therefore,

$$\psi_{2p_{+1}} = \frac{1}{8\left(a_0^5\pi\right)^{1/2}} r e^{-r/(2a_0)} \sin\theta e^{i\phi}$$

10.4: A Brief Introduction to Probability

We have talked about the fact that the wavefunction can be interpreted as a probability, but this is a good time to formalize some concepts and understand what we really mean by that.

Let's start by reviewing (or learning) a few concepts in probability theory. First, a random variable is a variable whose value is subject to variations due to chance. For example, we could define a variable that equals the number of days that it rains in Phoenix every month, or the outcome of throwing a die (the number of dots facing up), or the time it takes for the next bus to arrive to the bus station, or the waiting time we will have to endure next time we call a customer service phone line. Some of these random variables are discrete; the number of rain days or the number of dots facing up in a die can take on only a countable number of distinct values. For the case of the die, the outcome can only be $\{1,2,3,4,5,6\}$ In contrast, a waiting time is a continuous random variable. If you could measure with enough precision, the random variable can take any positive real value. Coming back to physical chemistry, the position of an electron in an atom or molecule is a good example of a continuous random variable.

Imagine a (admittedly silly) game that involves flipping two coins. You get one point for each tail, and two points for each head. The game has three possible outcomes: 2 points (if you get two tails), 3 points (if you get one tail and one head) and 4 points (if you get two heads). The outcomes do not have the same probability. The probability of getting two heads or two tails is 1/4, while the probability that you get one head and one tail is 1/2. If we define a random variable (x) that equals the number of points you get in one round of the game, we can represent the probabilities of getting each possible outcome as:

x	2	3	4
$P(x)$	1/4	1/2	1/4

The collection of outcomes is called the *sample space*. In this case, the sample space is $\{2,3,4\}$. If we add $P(x)$ over the sample space we get, as expected, 1. In other words, the probability that you get an outcome that belongs to the sample space needs to be 1, which makes sense because we defined the sample space as the collection of all possible outcomes. If you think about an electron in an atom, and define the position in polar coordinates, r (the distance from the nucleus of the atom) is a random variable that can take any value from 0 to ∞. The sample space for the random variable r is the set of positive real numbers.

Coming back to our discrete variable x, our previous argument translates into

$$\sum_{sample\ space} P(x) = 1$$

Can we measure probabilities? Not exactly, but we can measure the frequency of each outcome if we repeat the experiment a large number of times. For example, if we play this game three times, we do not know how many times we'll get 2, 3 or 4 points. But if we play the game a very large number of times, we know that half the time we will get 3 points, a quarter of the time will get 2 points, and another quarter 4 points. The probability is the frequency of an outcome in the limit of an infinite number of trials. Formally, the frequency is defined as the number of times you obtain a given outcome divided for the total number of trials.

Now, even if we do not have any way of predicting the outcome of our random experiment (the silly game we described above), if you had to bet, you would not think it twice and bet on $x = 3$ (one head and one tail). The fact that a random variable does not have a predictable outcome does not mean we do not have information about the distribution of probabilities. Coming back to our atom, we will be able to predict the value of r at which the probability of finding the electron is highest, the average value of r, etc. Even if we know that r can take values up to ∞, we know that it is much more likely to find it very close to the nucleus (e.g. within an angstrom) than far away (e.g. one inch). No physical law forbids the electron to be 1 inch from the nucleus, but the probability of that happening is so tiny, that we do not even think about this possibility.

The Mean of a Discrete Distribution

Let's talk about the mean (or average) some more. What is exactly the average of a random variable? Coming back to our "game", it would be the average value of x you would get if you could play the game an infinite number of times. You could also ask the whole planet to play the game once, and that would accomplish the same. The planet does not have an infinite number of people, but the average you get with several billion trials of the random experiment (throwing two coins) should be pretty close to the real average. We will denote the average (also called the mean) with angular brackets: $\langle x\rangle$. Let's say that we play this game 10^9 times.

We expect 3 points half the time (frequency = $1/2$), or in this case, 5×10^8 times. We also expect 2 points or 4 points with a frequency of $1/4$, so in this case, 2.5×10^8 times. What is the average?

$$\langle x \rangle = \frac{1}{4} \times 2 + \frac{1}{2} \times 3 + \frac{1}{4} \times 4 = 3$$

On average, the billion people playing the game (or you playing it a billion times) should get 3 points. This happens to be the most probable outcome, but it does not need to be the case. For instance, if you just flip one coin, you can get 1 point or 2 points with equal probability, and the average will be 1.5, which is not the most probable outcome. In fact, it is not even a possible outcome!.

In general, it should make sense that for a discrete variable:

$$\langle x \rangle = \sum_{i=1}^{k} P(x_i) x_i \tag{10.4.1}$$

where the sum is performed over the whole sample space, which contains k elements. Here, x_i is each possible outcome, and $P(x_i)$ is the probability of obtaining that outcome (or the fraction of times you would obtain it if you were to perform a huge number of trials).

Continuous Variables

How do we translate everything we just said to a continuous variable? As an example, let's come back to the random variable r, which is defined as the distance of the electron in the hydrogen atom from its nucleus. As we will see shortly, the 1s electron in the hydrogen atom spends most of its time within a couple of angstroms from the nucleus. We may ask ourselves, what is the probability that the electron will be found exactly at 1Å from the nucleus? Mathematically, what is $P(r = 1 \text{ Å})$? The answer will disappoint you, but this probability is zero, and it is zero for any value of r. The electron needs to be somewhere, but the probability of finding it an any particular value of r is zero? Yes, that is precisely the case, and it is a consequence of r being a continuous variable. Imagine that you get a random real number in the interval [0,1] (you could do this even in your calculator), and I ask you what is the probability that you get exactly $\pi/4$. There are infinite real numbers in this interval, and all of them are equally probable, so the probability of getting each of them is $1/\infty = 0$. Talking about the probabilities of particular outcomes is not very useful in the context of continuous variables. All the outcomes have a probability of zero, even if we intuitively know that the probability of finding the electron within 1Å is much larger than the probability of finding it at several miles. Instead, we will talk about the density of probability ($p(r)$). If you are confused about why the probability of a particular outcome is zero check the video listed at the end of this section.

A plot of $p(r)$ is shown in Figure $10.4.1$ for the case of the 1s orbital of the hydrogen atom. Again, we stress that $p(r)$ does not measure the probability corresponding to each value of r (which is zero for all values of r), but instead, it measures a probability density. We already introduced this idea in page

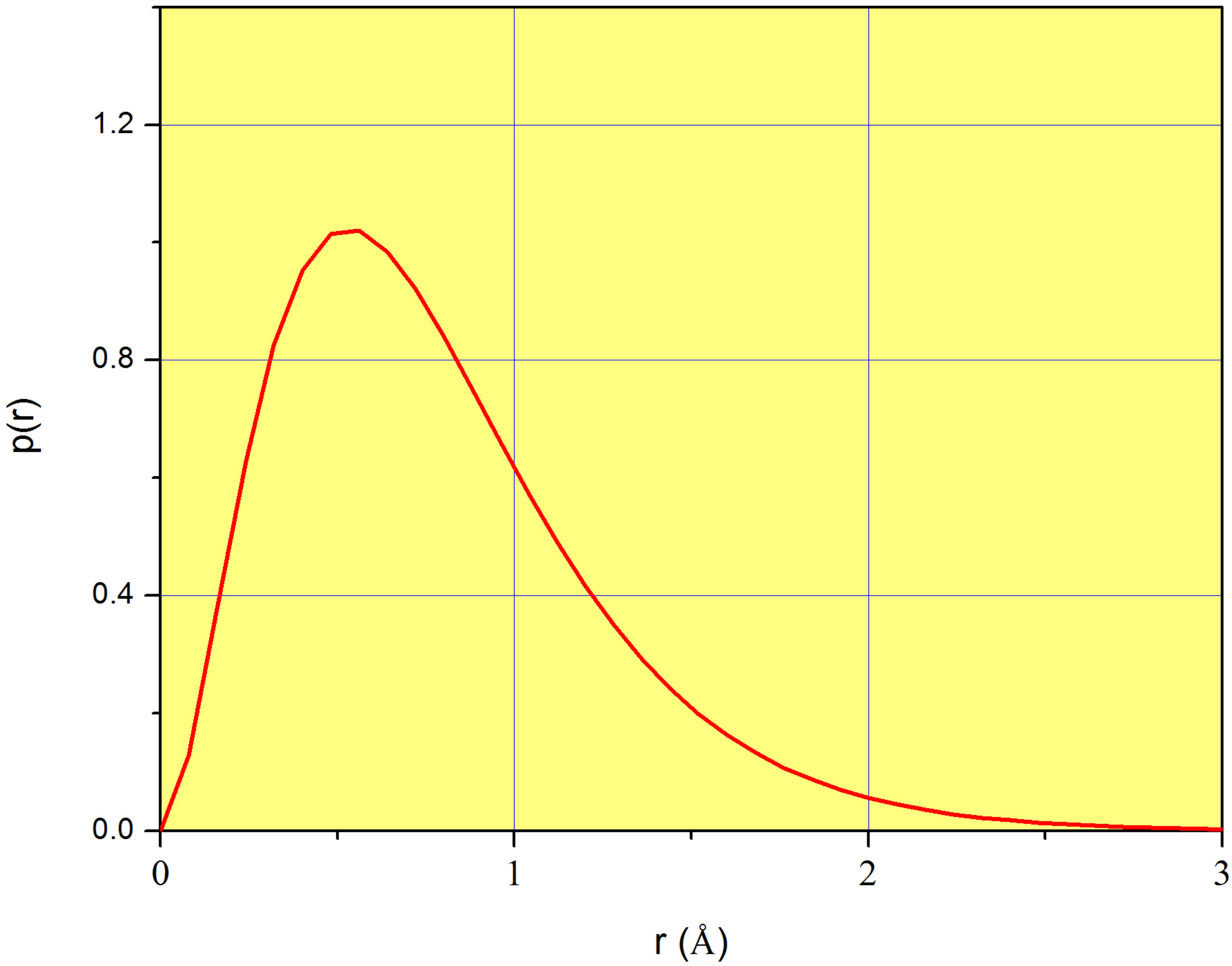


Figure 10.4.1: Radial density function ($p(r)$) for the 1s orbital of the hydrogen atom (CC BY-NC-SA; Marcia Levitus)

Formally, the probability density function ($p(r)$), is defined in this way:

$$P(a \leq r \leq b) = \int_a^b p(r)dr \tag{10.4.2}$$

This means that the probability that the random variable r takes a value in the interval $[a, b]$ is the integral of the probability density function from a to b. For a very small interval:

$$P(a \leq r \leq a + dr) = p(a)dr \tag{10.4.3}$$

In conclusion, although $p(r)$ alone does not mean anything physically, $p(r)dr$ is the probability that the variable r takes a value in the interval between r and $r + dr$. For example, coming back to Figure 10.4.1, $p(1$ Å$)$ = 0.62, which does not mean at all that 62% of the time we'll find the electron at exactly 1Å from the nucleus. Instead, we can use it to calculate the probability that the electron is found in a very narrow region around 1Å. For example, $P(1 \leq r \leq 1.001) \approx 0.62 \times 0.001 = 6.2 \times 10^{-4}$. This is only an approximation because the number 0.001, although much smaller than 1, is not an infinitesimal.

In general, the concept of probability density function is easier to understand in the context of Equation 10.4.2. You can calculate the probability that the electron is found at a distance shorter than 1Å as:

$$P(0 \leq r \leq 1) = \int_0^1 p(r)dr$$

and at a distance larger than 1Å but shorter than 2Å as

$$P(1 \leq r \leq 2) = \int_{1}^{2} p(r) dr$$

Of course the probability that the electron is somewhere in the universe is 1, so:

$$P(0 \leq r \leq \infty) = \int_{0}^{\infty} p(r) dr = 1$$

We haven't written $p(r)$ explicitly yet, but we will do so shortly so we can perform all these integrations and get the probabilities discussed above.

> Confused about continuous probability density functions? This video may help! http: //tinyurl.com/m6tgoap

The Mean of a Continuous Distribution

For a continuous random variable x, Equation 10.4.1 becomes:

$$\langle x \rangle = \int_{all\ outcomes} p(x) x\ dx \tag{10.4.4}$$

Coming back to our atom:

$$\langle r \rangle = \int_{0}^{\infty} p(r) r\ dr \tag{10.4.5}$$

Again, we will come back to this equation once we obtain the expression for $p(r)$ we need. But before doing so, let's expand this discussion to more variables. So far, we have limited our discussion to one coordinate, so the quantity $P(a \leq r \leq b) = \int_{a}^{b} p(r) dr$ represents the probability that the coordinate r takes a value between a and b, independently of the values of θ and ϕ. This region of space is the spherical shell represented in Figure $10.4.2$ in light blue. The spheres in the figure are cut for clarity, but of course we refer to the whole shell that is defined as the region between two concentric spheres of radii a and b.

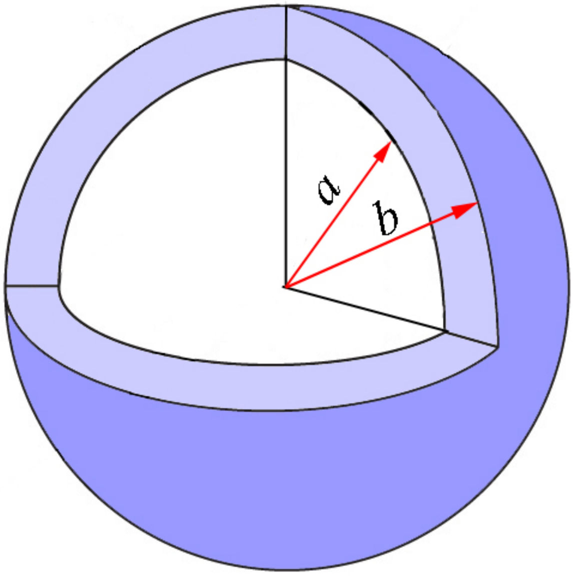


Figure 10.4.2: A spherical shell (CC BY-NC-SA; Marcia Levitus)

What if we are interested in the angles as well? Let's say that we want the probability that the electron is found between r_1 and r_2, θ_1 and θ_2, and ϕ_1 and ϕ_2. This volume is shown in Figure $10.4.3$. The probability we are interested in is:

$$P(r_1 \leq r \leq r_2, \theta_1 \leq \theta \leq \theta_2, \phi_1 \leq \phi \leq \phi_2) = \int_{\phi_1}^{\phi_2} \int_{\theta_1}^{\theta_2} \int_{r_1}^{r_2} p(r,\theta,\phi)\ r^2 \sin\theta dr d\theta d\phi$$

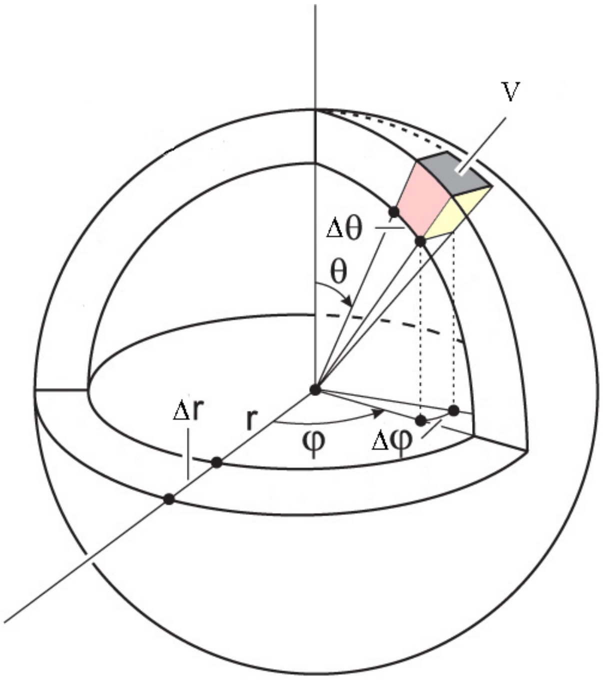


Figure 10.4.3: A volume delimited by the coordinates r and $r+\Delta r$, θ and $\theta+\Delta\theta$, and ϕ and $\phi+\Delta\phi$, (CC BY-NC-SA; Marcia Levitus)

Notice that we are integrating in spherical coordinates, so we need to use the corresponding differential of volume.

This probability density function, $p(r,\theta,\phi)$, is exactly what $|\psi(r,\theta,\phi)|^2$ represents! This is why we've been saying that $|\psi(r,\theta,\phi)|^2$ is a probability density. The function $|\psi(r,\theta,\phi)|^2$ does not represent a probability in itself, but it does when integrated between the limits of interest. Suppose we want to know the probability that the electron in the 1s orbital of the hydrogen atom is found between r_1 and r_2, θ_1 and θ_2, and ϕ_1 and ϕ_2. The answer to this question is:

$$\int_{\phi_1}^{\phi_2}\int_{\theta_1}^{\theta_2}\int_{r_1}^{r_2} |\psi_{1s}|^2\, r^2 \sin\theta dr d\theta d\phi$$

Coming back to the case shown in Figure $10.4.2$, the probability that r takes a value between a and b independently of the values of the angles, is the probability that r lies between a and b, and θ takes a value between 0 and π, and ϕ takes a value between 0 and 2π:

$$P(a\leq r\leq b)=P(a\leq r\leq b, 0\leq\theta\leq\pi, 0\leq\phi\leq 2\pi)=\int_0^{2\pi}\int_0^{\pi}\int_a^b |\psi_{1s}|^2\, r^2 \sin\theta dr d\theta d\phi \tag{10.4.6}$$

The Radial Density Function

So far we established that $|\psi(r,\theta,\phi)|^2$ is a probability density function in spherical coordinates. We can perform triple integrals to calculate the probability of finding the electron in different regions of space (but not in a particular point!). It is often useful to know the likelihood of finding the electron in an orbital at any given distance away from the nucleus. This enables us to say at what distance from the nucleus the electron is most likely to be found, and also how tightly or loosely the electron is bound in a particular atom. This is expressed by the radial distribution function, $p(r)$, which is plotted in Figure $10.4.1$ for the 1s orbital of the hydrogen atom.

In other words, we want a version of $|\psi(r,\theta,\phi)|^2$ that is independent of the angles. This new function will be a function of r only, and can be used, among other things, to calculate the mean of r, the most probable value of r, the probability that r lies in a given range of distances, etc.

We already introduced this function in Equation 10.4.2. The question now is, how do we obtain $p(r)$ from $|\psi(r,\theta,\phi)|^2$? Let's compare Equation 10.4.2 with Equation 10.4.6:

$$P(a\leq r\leq b)=\int_a^b p(r)dr$$

$$P(a\leq r\leq b)=P(a\leq r\leq b, 0\leq\theta\leq\pi, 0\leq\phi\leq 2\pi)=\int_0^{2\pi}\int_0^{\pi}\int_a^b |\psi(r,\theta,\phi)|^2\, r^2 \sin\theta dr d\theta d\phi$$

We conclude that

$$\int_a^b p(r)dr=\int_0^{2\pi}\int_0^{\pi}\int_a^b |\psi(r,\theta,\phi)|^2\, r^2 \sin\theta dr d\theta d\phi$$

All s orbitals are real functions of r only, so $|\psi(r,\theta,\phi)|^2$ does not depend on θ or ϕ. In this case:

$$\int_a^b p(r)dr=\int_0^{2\pi}\int_0^{\pi}\int_a^b \psi^2(r)\, r^2 \sin\theta dr d\theta d\phi=\int_0^{2\pi} d\phi\int_0^{\pi}\sin\theta\, d\theta\int_a^b \psi^2(r)\, r^2 dr=4\pi\int_a^b \psi^2(r)\, r^2 dr$$

Therefore, for an s orbital,

$$p(r)=4\pi\psi^2(r)\, r^2$$

For example, the normalized wavefunction of the 1s orbital is the solution of Example 10.1: $\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$. Therefore, for the 1s orbital:

$$p(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0} \tag{10.4.7}$$

Equation 10.4.7 is plotted in Figure 10.4.1. In order to create this plot, we need the value of a_0, which is a constant known as Bohr radius, and equals $5.29 \times 10^{-11} m$ (or 0.526 Å). Look at the position of the maximum of $p(r)$; it is slightly above 0.5Å and more precisely, exactly at $r = a_0$! Now it is clear why a_0 is known as a radius: it is the distance from the nucleus at which finding the only electron of the hydrogen atom is greatest. In a way, a_0 is the radius of the atom, although we know this is not strictly true because the electron is not orbiting at a fixed r as scientists believed a long time ago.

In general, for any type of orbital,

$$\int_a^b p(r)dr = \int_0^{2\pi}\int_0^{\pi}\int_a^b |\psi(r,\theta,\phi)|^2 \; r^2 \sin\theta dr d\theta d\phi = \int_a^b \int_0^{2\pi}\int_0^{\pi} |\psi(r,\theta,\phi)|^2 \; r^2 \sin\theta \; d\theta d\phi dr$$

in the right side of the equation, we just changed the order of integration to have dr last, and color coded the expression so we can easily identify $p(r)$ as:

$$p(r) = \int_0^{2\pi}\int_0^{\pi} |\psi(r,\theta,\phi)|^2 \; r^2 \sin\theta \; d\theta d\phi \tag{10.4.8}$$

Equation 10.4.8 is the mathematical formulation of what we wanted: a probability density function that does not depend on the angles. We integrate ϕ and θ so what we are left with represents the dependence with r.

We can multiply both sides by r:

$$rp(r) = r\int_0^{2\pi}\int_0^{\pi} |\psi(r,\theta,\phi)|^2 r^2 \sin\theta \; d\theta d\phi = \int_0^{2\pi}\int_0^{\pi} |\psi(r,\theta,\phi)|^2 r r^2 \sin\theta \; d\theta d\phi$$

and use Equation 10.4.5 to calculate $\langle r \rangle$

$$\langle r \rangle = \int_0^{\infty} p(r) r \; dr = \int_0^{\infty}\int_0^{2\pi}\int_0^{\pi} |\psi(r,\theta,\phi)|^2 r \; r^2 \sin\theta \; d\theta d\phi dr \tag{10.4.9}$$

The colors in these expressions are aimed to help you track where the different terms come from.

Let's look at Equation 10.4.9 more closely. Basically, we just concluded that:

$$\langle r \rangle = \int_{all \; space} |\psi|^2 r \; dV \tag{10.4.10}$$

where dV is the differential of volume in spherical coordinates. We know that ψ is normalized, so

$$\int_{all \; space} |\psi|^2 \; dV = 1$$

If we multiply the integrand by r, we get $\langle r \rangle$. We will discuss an extension of this idea when we talk about operators. For now, let's use Equation 10.4.10 to calculate $\langle r \rangle$ for the 1s orbital.

Example 10.4.1

Calculate the average value of r, $\langle r\rangle$, for an electron in the 1s orbital of the hydrogen atom. The normalized wavefunction of the 1s orbital, expressed in spherical coordinates, is:

$$\psi_{1s}=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

Solution

The average value of r is:

$$\langle r\rangle=\int_0^\infty p(r)r\,dr$$

or

$$\langle r\rangle=\int_{all\ space}|\psi|^2 r\,dV$$

The difference between the first expression and the second expression is that in the first case, we already integrated over the angles θ and ϕ. The second expression is a triple integral because $|\psi|^2$ still retains the angular information.

We do not have $p(r)$, so either we obtain it first from $|\psi|^2$, or directly use $|\psi|^2$ and perform the triple integration:

$$\langle r\rangle=\int_0^\infty\int_0^{2\pi}\int_0^\pi|\psi(r,\theta,\phi)|^2 r\ r^2\sin\theta\ d\theta d\phi dr$$

The expression highlighted in red is the differential of volume.

For this orbital,

$$|\psi(r,\theta,\phi)|^2=\frac{1}{\pi a_0^3}e^{-2r/a_0}$$

and then,

$$\langle r\rangle=\frac{1}{\pi a_0^3}\int_0^\infty e^{-2r/a_0}r^3\ dr\int_0^{2\pi}d\phi\int_0^\pi\sin\theta\ d\theta=\frac{4}{a_0^3}\int_0^\infty e^{-2r/a_0}r^3\ dr$$

From the formula sheet:

$\int_0^\infty x^n e^{-ax}dx=\frac{n!}{a^{n+1}}$, $a>0, n$ is a positive integer.

Here, $n=3$ and $a=2/a_0$.

$$\frac{4}{a_0^3}\int_0^\infty r^3e^{-2r/a_0}\ dr=\frac{4}{a_0^3}\times\frac{3!}{(2/a_0)^4}=\frac{3}{2}a_0$$

$$\langle r\rangle=\frac{3}{2}a_0$$

From Example 10.4.1, we notice that on average we expect to see the electron at a distance from the nucleus equal to 1.5 times a_0. This means that if you could measure r, and you perform this measurement on a large number of atoms of hydrogen, or on the same atom many times, you would, on average, see the electron at a distance from the nucleus $r=1.5a_0$. However, the probability of seeing the electron is greatest at $r=a_0$ (page). We see that the average of a distribution does not necessarily need to equal the value at which the probability is highest[2].

10.5: Problems

Problem 10.5.1

The wave function describing the state of an electron in the 1s orbital of the hydrogen atom is:

$$\psi_{1s} = Ae^{-r/a_0},$$

where a_0 is Bohr's radius (units of distance), and A is a normalization constant.

1. Calculate A
2. calculate $\langle r \rangle$, the average value of the distance of the electron from the nucleus.
3. The radius of the hydrogen atom is taken as the most probable value of r for the 1s orbital. Calculate the radius of the hydrogen atom.
4. What is the probability that the electron is found at a distance from the nucleus equal to $a_0/2$?
5. What is the probability that the electron is found at a distance from the nucleus less than $a_0/2$?
6. We know that the probability that the electron is found at a distance from the nucleus $0 < r < \infty$ is 1. Using this fact and the result of the previous question, calculate the probability that the electron is found at a distance from the nucleus greater than $a_0/2$.

Hint: $\int x^2 e^{ax} dx = e^{ax} \frac{(2-2ax+a^2x^2)}{a^3}$

Note: Be sure you show all the steps!

Problem 10.5.2

The wave function describing the state of an electron in the 2s orbital of the hydrogen atom is:

$$\psi_{2s} = Ae^{-r/2a_0}\left(2-\frac{r}{a_0}\right)$$

where a_0 is Bohr's radius (units of distance), and A is a normalization constant.

- Calculate A
- Calculate $\langle r \rangle$, the average value of the distance of the electron from the nucleus.

Problem 10.5.3

Calculate the normalization constant of each of the following orbitals:

$$\psi_{2p+1} = A_1 r e^{-r/2a_0} \sin\theta e^{i\phi}$$

$$\psi_{2p-1} = A_2 r e^{-r/2a_0} \sin\theta e^{-i\phi}$$

---

[1] The integral in r was solved using the formula sheet

[2] If you find this strange think about a situation where 20 18-year olds gather in a room with 4 60-year olds. The average age in the room is 25, but the most probable age is 18

CHAPTER OVERVIEW

11: Operators

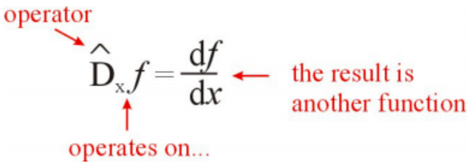
Chapter Objectives

- Understand the concept of a mathematical operator.
- Understand how to identify whether an operator is linear or not.
- Understand the concept of eigenfunction and eigenvalue of an operator.
- Learn how to perform algebraic operations with operators.
- Understand the concept of the commutator.
- Learn how to use operators in the context of quantum mechanics.

11.1: Definitions

Mathematical Operators

A mathematical operator is a symbol standing for a mathematical operation or rule that transforms one object (function, vector, etc) into another object of the same type. For example, when the derivative operator d/dx, also denoted by $\hat{D}_x$, operates on a function $f(x)$, the result is the function df/dx.



We can apply the operator $\hat{D}_x$ to any function. For example, let's consider the function $g(x) = 2\cos x + e^x$:

$$\hat{D}_x g(x) = -2\sin x + e^x$$

In physical chemistry, most operators involve either differentiation or multiplication. For instance, the multiplication operator denoted by $\hat{x}$ means "multiply by x". Using the previous example, when $\hat{x}$ operates on $g(x)$ we get

$$\hat{x}g(x) = 2x\cos x + xe^x$$

Before discussing what operators are good for, lets go over a few more examples. First, notice that we denote operators with a "hat". Let's define an operator $\hat{A}$ (read as "A hat") as $\hat{x} + \frac{d}{dx}$

$$\hat{A} = \hat{x} + \frac{d}{dx} \tag{11.1.1}$$

This reads as "multiply the function by x and add the result to the first derivative of the function with respect to x". The second term is equivalent to the operator we defined before, $\hat{D}_x$, and using one or the other is a matter of preference. Notice that the expression $\frac{d}{dx}$ does not require a "hat" because it is unambiguous. In the case of x, we need to use the "hat" to be sure we distinguish the operator (multiply by x) from the variable x. In the case of $\frac{d}{dx}$, the expression clearly needs to be applied to a function, so it is obviously an operator. When $\hat{A}$ operates on the function $g(x)$ (defined above), we obtain:

$$\hat{A}g(x) = \hat{x}g(x) + \frac{dg}{dx} = -2\sin x + e^x + 2x\cos x + xe^x$$

Linear Operators

In quantum mechanics we deal only with linear operators. An operator is said to be linear if

$$\hat{A}(c_1 f_1(x) + c_2 f_2(x)) = \hat{A}c_1 f_1(x) + \hat{A}c_2 f_2(x)$$

where c_1 and c_2 are constants (real or complex).

For instance, the $\frac{d}{dx}$ operator is linear:

$$\frac{d}{dx}(c_1 f_1(x) + c_2 f_2(x)) = \frac{d}{dx}c_1 f_1(x) + \frac{d}{dx}c_2 f_2(x)$$

If we define the operator $\hat{B}$ as the "square" operator (take the square of...), we notice that $\hat{B}$ is not linear because

$$\hat{B}(c_1 f_1(x) + c_2 f_2(x)) = (c_1 f_1(x))^2 + (c_2 f_2(x))^2 + 2c_1 f_1(x) c_2 f_2(x)$$

which is clearly different from

$$\hat{B}(c_1 f_1(x)) + \hat{B}(c_2 f_2(x)) = (c_1 f_1(x))^2 + (c_2 f_2(x))^2$$

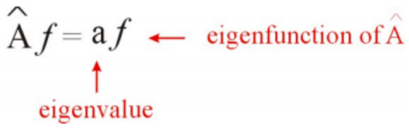
Eigenfunctions and Eigenvalues

A common problem in quantum mechanics is finding the functions (f) and constants (a) that satisfy

$$\hat{A}f = af \tag{11.1.2}$$

We will discuss the physical meaning of these functions and these constants later. For now, we will define the concept of eigenfunction and eigenvalue as follows:

If the result of operating on a function is the same function multiplied by a constant, the function is called an eigenfunction of that operator, and the proportionality constant is called an eigenvalue.



We can test whether a particular function is an eigenfunction of a given operator or not. For instance, let's consider the operator $-\frac{d^2}{dx^2}$ and the function $g(x)$ defined in page . Is $g(x)$ an eigenfunction of $-\frac{d^2}{dx^2}$? In lay terms: if we take the second derivative of $g(x)$ and change the sign of the result, do we get a function that can be expressed as $g(x)$ times a constant?

Let's try it:

$$-\frac{d^2g(x)}{dx^2} = 2\cos x - e^x$$

The result cannot be expressed as a constant times $g(x)$:

$$2\cos x - e^x \neq a(2\cos x + e^x)$$

so $g(x)$ is not an eigenfunction of the operator $-\frac{d^2}{dx^2}$.

Let's consider another function: $h(x) = 2sin(bx)$, where b is a constant. Is $h(x)$ and eigenfunction of the operator $-\frac{d^2}{dx^2}$? We'll take the second derivative of $g(x)$, multiply by -1, and check whether the result can be expressed as a constant times $h(x)$:

$$-\frac{d^2h(x)}{dx^2} = 2b^2\sin(bx)$$

Notice that the result is b^2 times the function $h(x)$, so the conclusion is that $h(x)$ is an eigenfunction of the operator $-\frac{d^2}{dx^2}$, and that the corresponding eigenvalue is b^2. *A common mistake is to conclude that the eigenvalue is* $2b^2$. *Be sure you understand why this is wrong.*. Also, notice that b^2 is a constant because it does not involve the variable x. *Another common mistake is to write eigenvalues that are not constants, but contain the independent variable.*

So far we have learned how to test whether a given function is an eigenfunction of a given operator or not. How can we calculate the eigenfunctions of a given operator? In general, this involves solving a differential equation. For instance, the eigenfunctions of the operator $-\frac{d^2}{dx^2}$ satisfy the equation

$$-\frac{d^2f(x)}{dx^2} = af(x),$$

where a is the eigenvalue. This is an ordinary second order differential equation with constant coefficients, so it can be solved with the methods we learned in previous chapters. Can you solve it and find the eigenfunctions of the operator $-\frac{d^2}{dx^2}$?

The eigenfunctions and eigenvalues of an operator play a central role in quantum mechanics. Before moving on, we'll introduce an important property that you will use often in your physical chemistry course:

If two functions $f_1(x)$ and $f_2(x)$ are both eigenfunctions of an operator with the same eigenvalue, the linear combination $c_1 f_1(x) + c_2 f_2(x)$ will also be an eigenfunction with the same eigenvalue.

For instance, the functions e^{ax} and e^{-ax} are both eigenfunctions of the operator $\frac{d^2}{dx^2}$ with eigenvalue a^2. Therefore, any linear combination $c_1 e^{ax} + c_2 e^{-ax}$ will be an eigenfunction of this operator with eigenvalue a^2, regardless of the values of c_1 and c_2. To prove it, take the second derivative of the function $c_1 e^{ax} + c_2 e^{-ax}$ and prove that it equals a^2 times $c_1 e^{ax} + c_2 e^{-ax}$.

The function $\cos(ax)$ is also an eigenfunction of $\frac{d^2}{dx^2}$. However, the function $c_1 e^{ax} + c_2 \cos(ax)$ is not. What went wrong?

11.2: Operator Algebra

Let's start by defining the identity operator, usually denoted by $\hat{E}$ or $\hat{I}$. The identity operator leaves the element on which it operates unchanged: $\hat{E}f(x)=f(x)$. This is analogous to multiplying by the number 1.

We can add operators as follows:

$$(\hat{A}+\hat{B})f=\hat{A}f+\hat{B}f.$$

For example,

$$\left(\hat{x}+\frac{d}{dx}\right)f=\hat{x}f+\frac{df}{dx}=xf+\frac{df}{dx}$$

(remember that $\hat{x}$ means "multiply by x").

The product between two operators is defined as the successive operation of the operators, with the one on the right operating first. For example,

$$\left(\hat{x}\frac{d}{dx}\right)f=\hat{x}\left(\frac{df}{dx}\right)=x\frac{df}{dx}. \tag{11.2.1}$$

We first apply the operator on the right (in this case "take the derivative of the function with respect to x"), and then the operator on the left ("multiply by x whatever you got in the first step"). We can use this definition to calculate the square of an operator. For example, if we define the operator $\hat{A}$ as $\hat{A}=\frac{d}{dx}$, the operator $\hat{A}^2$ is

$$\hat{A}\hat{A}=\frac{d}{dx}\frac{d}{dx}=\frac{d^2}{dx^2}. \tag{11.2.2}$$

Operator multiplication is not, in general, commutative: $\hat{A}\hat{B}\neq\hat{B}\hat{A}$. In other words, in general, the order of the operations matters. Before, we saw that $(\hat{x}\frac{d}{dx})f=x\frac{df}{dx}$. Let's revert the order of the operation: $(\frac{d}{dx}\hat{x})f$. Now, we first multiply the function by x and then take the derivative of the result:

$$\left(\frac{d}{dx}\hat{x}\right)f=\frac{d}{dx}(xf)=x\frac{df}{dx}+f. \tag{11.2.3}$$

In the last step, we calculated the derivative of the product using the differentiation rules we are familiar with.

We just proved that $\hat{x}\frac{d}{dx}\neq\frac{d}{dx}\hat{x}$, or in other words, the order in which we apply these two operators matters (i.e. whether we first take the derivative and then multiply by x, or first multiply by x and then take the derivative). Whether order matters or not has very important consequences in quantum mechanics, so it is useful to define the so-called commutator, defined as

$$[\hat{A},\hat{B}]=\hat{A}\hat{B}-\hat{B}\hat{A}. \tag{11.2.4}$$

For example, the commutator of the operators $\hat{x}$ and $\frac{d}{dx}$, denoted by $[\hat{x},\frac{d}{dx}]$, is by definition $\hat{x}\frac{d}{dx}-\frac{d}{dx}\hat{x}$. When $[\hat{A},\hat{B}]=0$, the operators $\hat{A}$ and $\hat{B}$ are said to commute. Therefore, if the operators $\hat{A}$ and $\hat{B}$ commute, then $\hat{A}\hat{B}=\hat{B}\hat{A}$. When the operators $\hat{A}$ and $\hat{B}$ do not commute, $\hat{A}\hat{B}\neq\hat{B}\hat{A}$, and the commutator $[\hat{A},\hat{B}]\neq 0$.

Before we move on, it is important to recognize that the product of two operators is also an operator. For instance, let's consider the product $\frac{d}{dx}\hat{x}$. This is an operator that, when applied to a function f, gives a new function $x\frac{df}{dx}+f$. For example, if $f=\sin(kx)$, $\frac{d}{dx}\hat{x}f=kx\cos(kx)+\sin(kx)$. In addition, notice that the operator $\frac{d}{dx}\hat{x}$ can be expressed as $\hat{E}+\hat{x}\frac{d}{dx}$, where $\hat{E}$ is the identity operator. When the operator $\hat{E}+\hat{x}\frac{d}{dx}$ operates on a function f, the result is the function itself (multiplied by one) plus x times the derivative of the function, which is exactly what we get when we perform $\frac{d}{dx}\hat{x}f$.

$$\underbrace{\frac{d}{dx}\hat{x}}_{\text{an operator}} = \underbrace{\hat{E}+\hat{x}\frac{d}{dx}}_{\text{an operator}}$$

$$\left(\frac{d}{dx}\hat{x}\right)f = \underbrace{\left(\hat{E}+\hat{x}\frac{d}{dx}\right)}_{\text{an operator}}\underbrace{f}_{\text{a function}} = \underbrace{f+x\frac{df}{dx}}_{\text{another function}}$$

An operator operates on a function to give another function

Similarly, the commutator between two operators is also an operator:

In general...

$$\underbrace{[\hat{A},\hat{B}]}_{\text{an operator}} = \hat{A}\hat{B}-\hat{B}\hat{A}$$

$$\underbrace{[\hat{A},\hat{B}]}_{\text{an operator}}\underbrace{f}_{\text{a function}} = \underbrace{\hat{A}\hat{B}f-\hat{B}\hat{A}f}_{\text{another function}}$$

An operator operates on a function to give another function

Example...

$$\left[\hat{x},\frac{d}{dx}\right]=\hat{x}\frac{d}{dx}-\frac{d}{dx}\hat{x}$$

$$\left[\hat{x},\frac{d}{dx}\right]f=\left(\hat{x}\frac{d}{dx}\right)f-\left(\frac{d}{dx}\hat{x}\right)f$$

$$\underbrace{\left[\hat{x},\frac{d}{dx}\right]}_{\text{an operator}}\underbrace{f}_{\text{a function}}=x\frac{df}{dx}-\left[f+x\frac{df}{dx}\right]=\underbrace{-f}_{\text{another function}}$$

Note that in the example on the right side of the figure we demonstrated that the operator $[\hat{x},\frac{d}{dx}]$ equals the operator $-\hat{E}$ ("multiply by -1"). In other words, when the commutator $[\hat{x},\frac{d}{dx}]$ (an operator) operates on a function f, the result is $-f$. Because $[\hat{x},\frac{d}{dx}]\neq 0$, the operators $\hat{x}$ and $\frac{d}{dx}$ do not commute. This is directly related to the uncertainty principle, which (in its simplest form) states that the more precisely the position of some particle is determined, the less precisely its momentum can be known. We will see the connection between this statement and the commutator in a moment, and you will discuss this in a lot of detail in your future physical chemistry courses.

✓ Example 11.2.1

Find the commutator

$$\left[\hat{x}^2,\frac{d^2}{dx^2}\right]$$

Solution

Remember that the commutator is an operator, so your answer should be an operator as well (that is, it should not contain a function). To 'see' what the commutator does (so we can write the equivalent operator), we apply an arbitrary function:

$$\left[\hat{x}^2,\frac{d^2}{dx^2}\right]f=\hat{x}^2\frac{d^2}{dx^2}f-\frac{d^2}{dx^2}\hat{x}^2 f$$

Remember that when we have expressions such as $\frac{d^2}{dx^2}\hat{x}^2 f$ we need to go from right to left, that is, we first multiply by x^2 and only then take the second derivative.

$$\frac{d^2}{dx^2}\hat{x}^2 f = \frac{d^2(x^2 f)}{dx^2} = \frac{d\left(2xf + x^2\frac{df}{dx}\right)}{dx} = 2x\frac{df}{dx} + 2f + x^2\frac{d^2f}{dx^2} + 2x\frac{df}{dx} = 4x\frac{df}{dx} + 2f + x^2\frac{d^2f}{dx^2}$$

$$\left[\hat{x}^2, \frac{d^2}{dx^2}\right] f = \hat{x}^2\frac{d^2}{dx^2}f - \frac{d^2}{dx^2}\hat{x}^2 f = x^2\frac{d^2f}{dx^2} - \left(4x\frac{df}{dx} + 2f + x^2\frac{d^2f}{dx^2}\right) = -4x\frac{df}{dx} - 2f$$

$$\left[\hat{x}^2, \frac{d^2}{dx^2}\right] = -4\hat{x}\frac{d}{dx} - 2\hat{E}$$

Again, your result should be an operator, and therefore should not contain the function f. Because $[\hat{x}^2, \frac{d^2}{dx^2}] \neq 0$, the two operators do not commute.

Common mistakes:

- to write the commutator as $[\hat{x}^2, \frac{d^2}{dx^2}] = -4x\frac{df}{dx} - 2f$
- to use an actual function (e.g. $\sin x$) instead of an arbitrary function f

11.3: Operators and Quantum Mechanics - an Introduction

We have already discussed that the main postulate of quantum mechanics establishes that the state of a quantum mechanical system is specified by a function called *the wavefunction*. The wavefunction is a function of the coordinates of the particle (the position) and time. We often deal with *stationary states*, i.e. states whose energy does not depend on time. For example, at room temperature and in the absence of electromagnetic radiation such as UV light, the energy of the only electron in the hydrogen atom is constant (the energy of the 1s orbital). In this case, all the information about the state of the particle is contained in a time-independent function, $\psi(\mathbf{r})$, where $\mathbf{r}$ is a vector that defines the position of the particle. In spherical coordinates $\mathbf{r}$ is described in terms of r, θ and ϕ (note the difference between $\mathbf{r}$ and r). For example, the wavefunction that describes the 1s orbital is:

$$\psi(r,\theta,\phi)=\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-(r/a_0)} \tag{11.3.1}$$

Notice that in this particular case the wavefunction is independent of θ and ϕ. This makes sense because the 1s orbital has spherical symmetry, and therefore the probability of finding the electron in a particular region of space should depend on r only.

We also discussed one of the postulates of quantum mechanics: the function

$$|\psi(\mathbf{r})|^2 dV=\psi^*(\mathbf{r})\psi(\mathbf{r})dV$$

is the probability that the particle lies in the volume element dV located at $\mathbf{r}$. We will now introduce three additional postulates:

1. Each observable in classical mechanics has an associated operator in quantum mechanics. Examples of observables are position, momentum, kinetic energy, total energy, angular momentum, etc (Table $11.3.1$).
2. The outcomes of any measurement of the observable associated with the operator $\hat{A}$ are the eigenvalues a that satisfy the eigenvalue equation $\hat{A}f=af(11.1.2)$.
3. The average value of the observable corresponding to $\hat{A}$ is given by

$$\iiint_{-\infty}^{\infty}\psi^*\hat{A}\psi dV \tag{11.3.2}$$

where dV is the differential of volume in the coordinates used to express ψ. We can perform this operation in two dimensions (e.g. if a particle is confined to a plane) by replacing dV by dA and performing a double integral, or in one dimension, by performing a single integral and replacing dV by dx. In each case, we need to integrate over all space.

To illustrate these postulates let's consider the hydrogen atom again. The wavefunction for an electron in a 1s orbital is shown in Equation 11.3.1.

Quantum mechanical operators for some physical observables.

Observable	symbol in classical physics	Operator in QM	Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	multiply by $\mathbf{r}$
Momentum	p_x	$\hat{p}_x$	$-i\hbar\frac{\partial}{\partial x}$
	p_y	$\hat{p}_y$	$-i\hbar\frac{\partial}{\partial y}$
	p_z	$\hat{p}_z$	$-i\hbar\frac{\partial}{\partial z}$
Kinetic Energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})$
Potential Energy	V($\mathbf{r}$)	$\hat{V}(\mathbf{r})$	multiply by $\hat{V}(\mathbf{r})$
Total Energy	E	$\hat{H}$	$\hat{T}+\hat{V}$
Angular Momentum	l_x	$\hat{l}_x$	$-i\hbar(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y})$

Observable	symbol in classical physics	Operator in QM	Operation
	l_y	$\hat{l}_y$	$-i\hbar(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z})$
	l_z	$\hat{l}_z$	$-i\hbar(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x})$

Table $11.3.1$: Quantum mechanical operators for some physical observables.

Let's say that we are able to measure the distance of the electron from the nucleus (i.e. r). What will we measure? According to the postulates listed above, if the wavefunction of Equation 11.3.1 is an eigenfunction of the operator $\hat{r}$, then we will measure the corresponding eigenvalue. However, we can easily see that $\hat{r}\psi \neq a\psi$, since the operator r stands for "multiply by r", and $r\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-(r/a_0)} \neq a\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-(r/a_0)}$. Remember that a should be a constant in Equation 11.3.1, so it cannot be a function of the coordinates (r,θ,ϕ). The fact that ψ is not an eigenfunction of the operator $\hat{r}$ means that a measurement of the position of the particle will give a value that we cannot predict. In other words, the position of the particle is not quantized, and we cannot know the result of the measurement with certainty. This should not be surprising to us, since we know that electrons do not move around the nucleus in fixed orbits as chemists once thought. Instead, we can talk about the probability of finding the electron at different values of r. A measurement of the observable r can in principle yield any value from 0 to ∞, although of course different values of r will be observed with different probabilities (see Section 10.4). Although we cannot predict the outcome of a single observation, we can calculate the average value of a very large number of observations (formally an infinite number of observations). We already calculated the average $\langle r\rangle$ in Section 10.4. Let's do it again following the formalism of operators.

✓ Example 11.3.1

The wavefunction of the 1s orbital is expressed in polar coordinates as:

$$\psi(r,\theta,\phi)=\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-(r/a_0)}$$

Obtain $\langle r\rangle$.

Solution

For an observable A:

$$\langle A\rangle=\int_{all\ space}\psi^*\ \hat{A}\ \psi\ dV$$

For the observable r:

$$\langle r\rangle=\int_{all\ space}\psi^*\ \hat{r}\ \psi\ dV$$

where $\hat{r}$ is the operator that corresponds to the observable r. According to Table $11.3.1$, the operator r is "multiply by r". Therefore:

$$\langle r\rangle=\int_{all\ space}\psi^*\ r\ \psi\ dV$$

For the 1s orbital,

$$\psi=\psi^*=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$$

and then,

$$\langle r\rangle=\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}\,r\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}r^2\sin\theta\,dr\,d\theta\,d\psi$$

where ψ^* is shown in red, $\hat{r}$ in black, ψ in blue, and dV in green.

We already solved this integral in Example $10.4.1$, where we obtained

$$\langle r\rangle=\frac{1}{\pi a_0^3}\int_0^{\infty}e^{-2r/a_0}r^3\,dr\int_0^{2\pi}d\psi\int_0^{\pi}\sin\theta\,d\theta=\frac{4}{a_0^3}\int_0^{\infty}e^{-2r/a_0}r^3\,dr=\frac{3}{2}a_0$$

Therefore, the average value of r is $3/2a_0$. Remember that a_0 is a physical constant known as Bohr's radius, which is approximately 0.53 Å, where 1 Å(Angstrom) equals $10^{-10}m$.

Important: Because $\hat{r}$ is "multiply by r", and the wavefunction is real, the integrand becomes $r\psi^2$. However, you need to be careful when the operator involves derivatives. The integrand is the complex conjugate of the wavefunction multiplied by the function that you obtain when you calculate $\hat{A}\psi$. See Test Yourself 11.6 for an example where the order of the operations is important.

The result of Example $11.3.1$ shows that the average distance of a 1s electron from the nucleus is $3/2a_0$, which is about $8\times10^{-10}m$. The fact that the wavefunction is not an eigenfunction of the operator $\hat{r}$ tells us that we cannot predict the result of a measurement of the variable r. What about other observables such as kinetic energy or total energy?

Are the orbitals of the hydrogen atom eigenfunctions of the operator $\hat{T}$ (kinetic energy)? Let's try it with the 1s orbital of Equation 11.3.1 (our conclusion will be true for all other orbitals, as you will see in your advanced physical chemistry courses). Notice that the expressions of Table $11.3.1$ are written in cartesian coordinates, while the orbitals are expressed in spherical coordinates. We could express the orbitals in cartesian coordinates, but that would be a lot of work because, in principle, there are infinite orbitals. It is much wiser to express the operators in spherical coordinates, so we can use them any time we need them in a problem that is best described in this coordinate system. This can be done using the chain rule, as we saw in previous chapters. In spherical coordinates, the operator $\hat{T}$ is written as:

$$\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\tag{11.3.3}$$

where m is the mass of the particle (in this case the electron). If you compare this expression to the one found in Table $11.3.1$, you may think we are complicating ourselves unnecessarily. However, it would be much more time consuming to convert every wavefunction we want to work with to cartesian coordinates, while obtaining Equation 11.3.3 from the expression in Table $11.3.1$ is a one time job.

To see if the 1s orbital is an eigenfunction of the operator defined in Equation 11.3.3 we need to calculate

$$\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right)$$

and see if the result equals a constant times the function ψ. The problem is solved in Example $11.3.2$

✓ Example $11.3.2$

Decide whether the 1s orbital

$$\psi(r,\theta,\psi)=\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}e^{-(r/a_0)}$$

is an eigenfunction of the operator $\hat{T}$, defined in Equation 11.3.3.

Solution

The 1s orbital depends on r only, and therefore the derivatives with respect to θ and ϕ are zero (this will be true for all the s-orbitals). Therefore, Equation 11.3.3 reduces to:

$$\hat{T}=\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right)$$

The function ψ is an eigenfunction of $\hat{T}$ if the following relationship is true:

$$\hat{T}\psi=a\psi$$

Remember that a should be a constant (i.e. should not depend on r,θ,ψ.

Let's calculate $\hat{T}\psi$. We first need to calculate the derivative of ψ with respect to r, multiply the result by r^2, take the derivative with respect to r of the result, divide the result by r^2, and finally multiply the result by $-\hbar/2m$.

To simplify notation, lets call $A=\frac{1}{\sqrt{\pi}}\frac{1}{a_0^{3/2}}$, so that $\psi(r,\theta,\psi)=Ae^{-(r/a_0)}$.

$$\begin{aligned}
\frac{\partial\psi}{\partial r} &= -\frac{A}{a_0}e^{-(r/a_0)}\\
\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) &= \frac{\partial}{\partial r}\left(r^2\left(-\frac{A}{a_0}e^{-(r/a_0)}\right)\right)\\
&= -\frac{A}{a_0}\left(2re^{-(r/a_0)}-\frac{1}{a_0}r^2e^{-(r/a_0)}\right)\\
\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) &= -\frac{A}{a_0}\left(2\frac{1}{r}e^{-(r/a_0)}-\frac{1}{a_0}e^{-(r/a_0)}\right)\\
\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) &= \frac{A\hbar^2}{2ma_0}e^{-(r/a_0)}\left(\frac{2}{r}-\frac{1}{a_0}\right)\\
&= \frac{\hbar^2}{2ma_0}\left(\frac{2}{r}-\frac{1}{a_0}\right)\psi\neq a\psi
\end{aligned}$$

Therefore, ψ is not an eigenfunction of $\hat{T}$, and we cannot predict the result of a measurement of the kinetic energy.

We will now consider the total energy (that is, the sum of the kinetic energy plus the potential energy). Because this is such an important property, the corresponding operator has a special name: the Hamiltonian ($\hat{H}$). To write down the Hamiltonian, we need to add the kinetic energy operator (Equation 11.3.3) to the potential energy operator. However, in contrast to the kinetic energy term, the potential energy depends on the forces experienced by the particle, and therefore we cannot write a generic expression. If you took a physics course, you may be familiar with different expressions for the potential energy of different systems (e.g. two charged particles, a spring, a particle in a gravitational field, etc). In all cases, the potential energy depends on the coordinates of the particles. For example, for two charged point particles of opposite sign, the electrostatic potential associated with their interaction is $V(r)=kq_1q_2/r$. Here, k is a constant (see below), q_1 and q_2 are the charges of the two particles, and r is the distance that separates them. If you look at table [tab:operators], you will see that the operator that corresponds to this expression is just "multiply by...". This is because the potential energy depends on the coordinates, and not on the derivatives. Therefore, it is like the operator $\hat{r}$ we saw before. For the hydrogen atom, the potential energy arises from the interaction between the only electron and the only proton in the atom. Both have the same charge (in absolute value), but one is negative and the other one positive, so $q_1q_2=-\epsilon^2$, where ϵ is the charge of the proton. With this in mind, we can write the operator $\hat{V}$ as:

$$\hat{V}=-\frac{\epsilon^2}{4\pi\epsilon_0}\frac{1}{r}$$

It is important to understand that this is an operator which operates by "multiplying by...". Therefore $\hat{V}\psi=-\frac{\epsilon^2}{4\pi\epsilon_0}\frac{1}{r}\psi$. A common mistake is to forget the wavefunction ψ. The Hamiltonian for the hydrogen atom can then be expressed as the sum $\hat{T}+\hat{V}$:

$$\hat{H}=\frac{-\hbar^2}{2m}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)-\frac{\epsilon^2}{4\pi\epsilon_0}\frac{1}{r}\tag{11.3.4}$$

According to the postulates of quantum mechanics, if the wavefunction defined in Equation 11.3.1 is an eigenfunction of this Hamiltonian, every time we measure the total energy of the electron we will measure the corresponding eigenvalue. In other words, if this is true: $\hat{H}\psi = a\psi$, then the constant a is the energy of one electron in the 1s orbital. If we used the wavefunction for the 2s orbital instead, we would get the energy of the 2s orbital, and so on. It is important to note that the constants in the potential energy term are related to Bohr radius (a_0) as:

$$\frac{\epsilon^2}{4\pi\epsilon_0} = \frac{\hbar^2}{ma_0}.$$

This relationship will allow you to simplify your result.

11.4: Problems

Problem 11.4.1

Consider the operator $\hat{A}$ defined in Equation 11.1.1as $\hat{A} = \hat{x} + \frac{d}{dx}$. Is it linear or non-linear? Justify.

Problem 11.4.2

Which of these functions are eigenfunctions of the operator $-\frac{d^2}{dx^2}$? Give the corresponding eigenvalue when appropriate. In each case k can be regarded as a constant.

$$f_1(x) = e^{ikx}$$

$$f_2(x) = \cos(kx)$$

$$f_3(x) = e^{-kx^2}$$

$$f_4(x) = e^{ikx} - cos(kx)$$

Problem 11.4.3

In quantum mechanics, the x, y and z components of the angular momentum are represented by the following operators:

$$\begin{aligned}\hat{L}_x &= i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \frac{\cos\phi}{\tan\theta}\frac{\partial}{\partial\phi}\right)\\ \hat{L}_y &= i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \frac{\sin\phi}{\tan\theta}\frac{\partial}{\partial\phi}\right)\\ \hat{L}_z &= -i\hbar\left(\frac{\partial}{\partial\phi}\right)\end{aligned}$$

The operator for the square of the magnitude of the orbital angular momentum, $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ is:

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

a) Show that the three 2p orbitals of the H atom are eigenfunctions of both $\hat{L}^2$ and $\hat{L}_z$, and determine the corresponding eigenvalues.

$$\psi_{2p0} = \frac{1}{\sqrt{32\pi a_0^3}} r e^{-r/2a_0}\cos\theta$$

$$\psi_{2p+1} = \frac{1}{\sqrt{64\pi a_0^3}} r e^{-r/2a_0}\sin\theta e^{i\phi}$$

$$\psi_{2p-1} = \frac{1}{\sqrt{64\pi a_0^3}} r e^{-r/2a_0}\sin\theta e^{-i\phi}$$

b) Calculate $\hat{L}_x\psi_{2p0}$. Is ψ_{2p0} and eigenfunction of $\hat{L}_x$?

c) Calculate $\hat{L}_y\psi_{2p0}$. Is ψ_{2p0} and eigenfunction of $\hat{L}_y$?

? Problem 11.4.4

Prove that

$$\left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y$$

? Problem 11.4.5

For a system moving in one dimension, the momentum operator can be written as

$$\hat{p} = i\hbar\frac{d}{dx}$$

Find the commutator $[\hat{x}, \hat{p}]$

Note: $\hbar$ is defined as $h/2\pi$, where h is Plank's constant. It has been defined because the ratio $h/2\pi$ appears often in quantum mechanics.

? Problem 11.4.6

We demonstrated that $\psi_1 s$ is not an eigenfunction of $\hat{T}$. Yet, we can calculate the average kinetic energy of a 1s electron, $\langle T\rangle$. Use Equation $11.3.1$ to calculate an expression for $\langle T\rangle$.

? Problem 11.4.7

Use the Hamiltonian of Equation $11.3.5$ to calculate the energy of the electron in the 1s orbital of the hydrogen atom. The normalized wave function of the 1s orbital is:

$$\psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

? Problem 11.4.8

The expression of Equation $11.3.1$ can be used to obtain the expectation (or average) value of the observable represented by the operator $\hat{A}$.

The state of a particle confined in a one-dimensional box of length a is described by the following wavefunction:

$$\psi(x) = \begin{cases} \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right) & \text{if } 0 \leq x \leq a \\ 0 & \text{otherwise} \end{cases}$$

The momentum operator for a one-dimensional system was introduced in Problem $11.4.5$.

a) Obtain an expression for $\hat{p}^2$ and determine if ψ is an eigenfunction of $\hat{p}$ and $\hat{p}^2$. If possible, obtain the corresponding eigenvalues.

Hint: $\hat{p}^2$ is the product $\hat{p}\hat{p}$.

b) Determine if ψ is an eigenfuction of $\hat{x}$. If possible, obtain the corresponding eigenvalues.

c) Calculate the following expectation values: $\langle x\rangle$, $\langle p^2\rangle$, and $\langle p\rangle$. Compare with the eigenvalues calculated in the previous questions.

CHAPTER OVERVIEW

12: Partial Differential Equations

Objectives

- Learn the method of separation of variables to solve simple partial differential equations.
- Understand how to apply the method of separation of variables to two important problems in the physical sciences: The wave equation in one dimension and molecular diffusion.

12.1: Introduction to Partial Differential Equations

Many important equations in physical chemistry, engineering, and physics, describe how some physical quantity, such as a temperature or a concentration, varies with position and time. This means that one or more spatial variables and time serve as independent variables. For example, let's consider the concentration of a chemical around the point (x, y, z) at time t: $C = C(x, y, z, t)$. The differential equation that describes how C changes with time is

$$\nabla^2 C(x,y,z,t) = \frac{1}{D}\frac{\partial C(x,y,z,t)}{\partial t} \tag{12.1.1}$$

where ∇^2 is an operator known as the Laplacian. In cartesian three-dimensional coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

The constant D is the diffusion coefficient, and determines how far molecules move on average in a given period of time. The diffusion coefficient depends on the size and shape of the molecule, and the temperature and viscosity of the solvent.

The diffusion equation (Equation 12.1.1) is a partial differential equation because the dependent variable, C, depends on more than one independent variable, and therefore its partial derivatives appear in the equation.

Other important equations that are common in the physical sciences are:

The heat equation:

$$\nabla^2 T(x,y,z,t) = \frac{1}{\alpha}\frac{\partial T(x,y,z,t)}{\partial t} \tag{12.1.2}$$

which is in a way a diffusion equation, except that the quantity that diffuses is heat, and not matter. This translates into a change in temperature instead of a change in concentration.

The wave equation:

$$\nabla^2 u(x,y,z,t) = \frac{1}{v^2}\frac{\partial^2 u(x,y,z,t)}{\partial t^2} \tag{12.1.3}$$

which describes the displacement of all points of a vibrating thin string. Here, v has units of speed, and it's related to the elasticity of the string.

The time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) + V\psi(x,y,z) = E\psi(x,y,z) \tag{12.1.4}$$

which we have already introduced in previous chapters. Note that the Schrödinger equation becomes an Ordinary Differential Equation for one-dimensional problems (e.g. the one-dimensional particle in a box, page), but it is a PDE for systems where particles are allowed to move in two or more dimensions.

In this course, we will introduce the simplest examples of PDEs relevant to physical chemistry. As you will see, solving these equations analytically is rather complex, and the solutions depend greatly on initial and boundary conditions. Because solving these equations is time consuming, in your upper-level physical chemistry courses your teacher will often show you the solutions without going through the whole derivation. Yet, it is important that you go through all the work at least once for the simplest cases, so you know what it is involved in solving the PDEs you will see in the future.

12.2: The Method of Separation of Variables

Most PDEs you will encounter in physical chemistry can be solved using a method called "separation of variables". We will exemplify the method by solving the easiest PDE: The Laplace equation in two dimensions:

$$\frac{\partial f(x,y)}{\partial x}+\frac{\partial f(x,y)}{\partial y}=0 \tag{12.2.1}$$

The solutions of Laplace's equation are important in many fields of science, including electromagnetism, astronomy, and fluid dynamics.

separation of variable Steps

The following steps summarize everything we have done to find the solution:

1. Assume that the solution of the differential equation can be expressed as the product of functions of each of the variables.
2. Group terms that depend on each of the independent variables (in this case x and y).
3. Identify the terms that need to equal constants.
4. Solve the ODEs (do not forget the integration constants!)
5. Put everything together. Your answer will have one or more constants that will eventually be determined from boundary conditions

Step 1

The first step in the method of separation of variables is to assume that the solution of the differential equation, in this case $f(x,y)$, can be expressed as the product of a function of x times a function of y.

$$f(x,y)=X(x)Y(y) \tag{12.2.2}$$

Don't get confused with the nomenclature. We use lower case to denote the variable, and upper case to denote the function. We could have written Eqution 12.2.2 as

$$f(x,y)=h(x)g(y)$$

Step 2

In the second step, we substitute $f(x,y)$ in Equation 12.2.1 by Equation 12.2.2:

$$\frac{\partial X(x)Y(y)}{\partial x}+\frac{\partial X(x)Y(y)}{\partial y}=0$$

$$Y(y)\frac{\partial X(x)}{\partial x}+X(x)\frac{\partial Y(y)}{\partial y}=0 \tag{12.2.3}$$

Step 3

The third step involves reorganizing the terms of Equation 12.2.3 so all terms in x and y are grouped together. There is no universal method for this step. In this example, we'll separate variables by dividing all terms by $X(x)Y(y)$, but in general you will need to figure out how to separate variables for the particular equation you are solving:

$$\frac{1}{X(x)}\frac{\partial X(x)}{\partial x}+\frac{1}{Y(y)}\frac{\partial Y(y)}{\partial y}=0 \tag{12.2.4}$$

Step 4

In the fourth step, we recognize that Equation 12.2.4 is the sum of two terms (it would be three if we were solving a problem in 3 dimensions), and each term depends on one variable only. In this case, the first term is a function of x only, and the second term is a function of y only. How can we add something that depends on x only to something that depends on y only and get zero? This sounds impossible, as terms in x will never cancel out terms in y [1].

The only way to make Equation 12.2.4 hold for any value of x and y is to force each summand to be a constant. The term $\frac{1}{X(x)}\frac{\partial X(x)}{\partial x}$ cannot be a function of x, and the term $\frac{1}{Y(y)}\frac{\partial Y(y)}{\partial y}$ cannot be a function of y:

$$\frac{1}{X(x)}\frac{\partial X(x)}{\partial x}=K_1 \tag{12.2.5}$$

$$\frac{1}{Y(y)}\frac{\partial Y(y)}{\partial y}=K_2 \tag{12.2.6}$$

This step transforms a PDE into two ODEs. In general, we will have one ODE for each independent variable. In this particular case, because the two terms need to add up to zero, we have $K_1=-K_2$.

Step 5

In the fifth step, we solve the 2 ODEs using the methods we learned in previous chapters. We will get $X(x)$ from Equation 12.2.5 and $Y(y)$ from Equation 12.2.6. Both solutions will contain arbitrary constants that we will evaluate using initial or boundary conditions if given. In this case, the two equations are mathematically identical, and are separable 1st order ordinary differential equations. The solutions (which you should be able to get on your own) are:

$$X(x)=Ae^{K_1x}$$

$$Y(y)=Be^{-K_1y}$$

Step 6

In step 6, we combine the one-variable solutions to obtain the many-variable solution we are looking for (Equation 12.2.2):

$$f(x,y)=X(x)Y(y)=Ae^{K_1x}Be^{-K_1y}=Ce^{K_1(x-y)}$$

where C is a constant.

We should always finish by checking that our answer indeed satisfies the PDE we were trying to solve:

$$\frac{\partial f(x,y)}{\partial x}+\frac{\partial f(x,y)}{\partial y}=0$$

$$f(x,y)=Ce^{K_1(x-y)}\rightarrow\frac{\partial f(x,y)}{\partial x}=CK_1e^{K_1(x-y)}$$

$$\frac{\partial f(x,y)}{\partial y}=-CK_1e^{K_1(x-y)}\rightarrow\frac{\partial f(x,y)}{\partial x}+\frac{\partial f(x,y)}{\partial y}=0$$

12.3: The Wave Equation in One Dimension

The wave equation is an important second-order linear partial differential equation that describes waves such as sound waves, light waves and water waves. In this course, we will focus on oscillations in one dimension. Let's consider a thin string of length l that is fixed at its two endpoints, and let's call the displacement of the string from its horizontal position $u(x,t)$ (figure [fig:pde1]). The displacement of each point in the string is limited to one dimension, but because the displacement also depends on time, the one-dimensional wave equation is a PDE:

$$\frac{\partial^2 u(x,t)}{\partial x^2}=\frac{1}{v^2}\frac{\partial^2 u(x,t)}{\partial t^2} \tag{12.3.1}$$

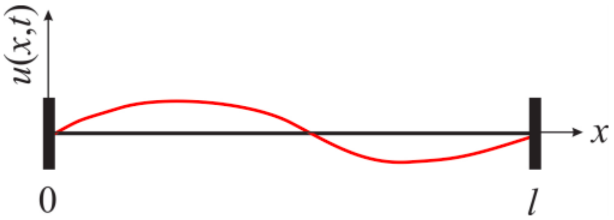


Figure 12.3.1: A vibrating string of length l held at both ends. (CC BY-NC-SA; Marcia Levitus)

Because the string is held at both ends, the PDE is subject to two boundary conditions:

$$u(0,t)=u(l,t)=0 \tag{12.3.2}$$

Using the method of separation of variables, we assume that the function $u(x,t)$ can be written as the product of a function of only x and a function of only t.

$$u(x,t)=f(x)g(t) \tag{12.3.3}$$

Substituting Equation 12.3.3in Equation 12.3.1:

$$\begin{aligned}\frac{\partial^2 f(x)g(t)}{\partial x^2}&=\frac{1}{v^2}\frac{\partial^2 f(x)g(t)}{\partial t^2}\\ g(t)\frac{\partial^2 f(x)}{\partial x^2}&=\frac{1}{v^2}f(x)\frac{\partial^2 g(t)}{\partial t^2}\end{aligned} \tag{12.3.4}$$

and separating the terms in x from the terms in y:

$$\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2}=\frac{1}{v^2}\frac{1}{g(t)}\frac{\partial^2 g(t)}{\partial t^2} \tag{12.3.5}$$

Remember that v is a constant, and we could leave it on either side of Equation 12.3.5. The left side of this equation is a function of x only, and the right side is a function of t only. Because x and t are independent variables, the only way that the equality holds is that each side equals a constant.

$$\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2}=\frac{1}{v^2}\frac{1}{g(t)}\frac{\partial^2 g(t)}{\partial t^2}=K$$

K is called the separation constant, and will be determined by the boundary conditions. Note that after separation of variables, one PDE became two ODEs:

$$\frac{1}{f(x)}\frac{\partial^2 f(x)}{\partial x^2}=K\rightarrow\frac{\partial^2 f(x)}{\partial x^2}-Kf(x)=0 \tag{12.3.6}$$

$$\frac{1}{v^2}\frac{1}{g(t)}\frac{\partial^2 g(t)}{\partial t^2}=K\rightarrow\frac{\partial^2 g(t)}{\partial t^2}-Kv^2g(t)=0 \tag{12.3.7}$$

These are both second order ordinary differential equations with constant coefficients, so we can solve them using the methods we learned in Chapter 5.

From Equation 12.3.6,

$$\frac{\partial^2 f(x)}{\partial x^2} - Kf(x) = 0$$

which is a 2nd order ODE with auxiliary equation

$$\alpha^2 - K = 0 \Rightarrow \alpha = \pm\sqrt{K}$$

and therefore

$$f(x) = c_1 e^{\sqrt{K}x} + c_2 e^{-\sqrt{K}x} \tag{12.3.8}$$

We do not know yet if K is positive, negative or zero, so we do not know if these are real or complex exponentials. We will use the boundary conditions ($f(0) = f(l) = 0$) and see what happens:

$$f(x) = c_1 e^{\sqrt{K}x} + c_2 e^{-\sqrt{K}x} \rightarrow f(0) = c_1 + c_2 = 0 \Rightarrow c_1 = -c_2$$

$$f(x) = c_1 (e^{\sqrt{K}x} - e^{-\sqrt{K}x}) \rightarrow f(l) = c_1 (e^{\sqrt{K}l} - e^{-\sqrt{K}l}) = 0$$

There are two ways to make

$$f(l) = c_1 (e^{\sqrt{K}l} - e^{-\sqrt{K}l}) = 0.$$

We could choose $c_1 = 0$, but this choice would result in $f(x) = 0$, which physically means the string is not vibrating at all (the displacement of all points is zero). This is certainly a mathematically acceptable solution, but it is not a solution that represents the physical behavior of our string. Therefore, the only viable choice is $e^{\sqrt{K}l} = e^{-\sqrt{K}l}$. Let's see what this means in terms of K. There is no positive value of K that makes

$$e^{\sqrt{K}l} = e^{-\sqrt{K}l}.$$

If $K = 0$, we obtain $f(x) = 0$, which is again not physically acceptable. Then, the value of K has to be negative, and $\sqrt{K}$ is an imaginary number:

$$e^{\sqrt{K}l} = e^{-\sqrt{K}l}$$

$$e^{i\sqrt{|K|}l} = e^{-i\sqrt{|K|}l}$$

where $|K| = -K$ is the absolute value of $K < 0$. Using Euler's relationship:

$$\cos(\sqrt{|K|}l) + i\sin(\sqrt{|K|}l) = \cos(\sqrt{|K|}l) - i\sin(\sqrt{|K|}l)$$

$$2i\sin(\sqrt{|K|}l) = 0 \rightarrow \sqrt{|K|}l = n\pi \rightarrow \sqrt{|K|} = \left(\frac{n\pi}{l}\right)$$

Now that we have an expression for K, we can write an expression for $f(x)$:

$$f(x) = c_1 (e^{\sqrt{K}x} - e^{-\sqrt{K}x}) = c_1 (e^{i\sqrt{|K|}x} - e^{-i\sqrt{|K|}x}) = 2ic_1 \sin(\sqrt{|K|}x)$$

$$f(x) = A\sin\left(\frac{n\pi}{l}x\right) \tag{12.3.9}$$

So far we got $f(x)$, so we need to move on and get an expression for $g(t)$ from Equation 12.3.7. Notice, however, that we now know the value of K, so let's re-write Equation 12.3.7 as:

$$\frac{\partial^2 g(t)}{\partial t^2} + \left(\frac{n\pi}{l}\right)^2 v^2 g(t) = 0 \tag{12.3.10}$$

This is another 2nd order ODE, with auxiliary equation

$$\alpha^2 + \left(\frac{n\pi}{l}\right)^2 v^2 = 0 \rightarrow \alpha = \pm i\left(\frac{n\pi}{l}v\right)$$

we can then write $g(t)$ as:

$$g(t)=c_1e^{i\left(\frac{n\pi}{l}v\right)t}+c_2e^{-i\left(\frac{n\pi}{l}v\right)t}$$

which you should be able to prove can be rewritten as

$$g(t)=c_3\sin\left(\frac{n\pi}{l}vt\right)+c_4\cos\left(\frac{n\pi}{l}vt\right) \tag{12.3.11}$$

We cannot get the values of c_3 and c_4 yet because we do not have information about initial conditions. Before discussing this, however, let's put the two pieces together:

$$u(x,t)=\sin\left(\frac{n\pi}{l}x\right)\left[p_n\sin\left(\frac{n\pi}{l}vt\right)+q_n\cos\left(\frac{n\pi}{l}vt\right)\right]$$

where we combined the constants A and $c_{1,2}$ and re-named them p_n and q_n. The subindices stress the fact that these constants depend on n, which will be important in a minute. Before we move on, and to simplify notation, let's recognize that the quantity $\frac{n\pi v}{l}$ has units of reciprocal time. This is true because it needs to give an dimensionless number when multiplied by t. This means that, physically, $\frac{n\pi v}{l}$ represents a frequency, so we can call it ω_n:

$$u(x,t)=\sin\left(\frac{n\pi}{l}x\right)\left[p_n\sin(\omega_nt)+q_n\cos(\omega_nt)\right]\;\; n=1,2,\ldots,\infty \tag{12.3.12}$$

At this point, we recognize that we have an infinite number of solutions:

$$\begin{aligned}u_1(x,t)&=\sin\left(\frac{\pi}{l}x\right)\left[p_1\sin(\omega_1t)+q_1\cos(\omega_1t)\right]\\ u_2(x,t)&=\sin\left(2\frac{\pi}{l}x\right)\left[p_2\sin(\omega_2t)+q_2\cos(\omega_2t)\right]\\ &\vdots\\ u_n(x,t)&=\sin\left(n\frac{\pi}{l}x\right)\left[p_n\sin(\omega_nt)+q_n\cos(\omega_nt)\right]\end{aligned} \tag{12.3.13}$$

where $\omega_1,\omega_2,\ldots,\omega_n=\frac{\pi v}{l},\frac{2\pi v}{l},\ldots,\frac{n\pi v}{l}$. As usual, the general solution is a linear combination of all these solutions:

$$u(x,t)=c_1u_1(x,t)+c_2u_2(x,t)+\ldots+c_nu_n(x,t)=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)\left[a_n\sin(\omega_nt)+b_n\cos(\omega_nt)\right] \tag{12.3.14}$$

where $a_n=c_np_n$ and $b_n=c_nq_n$.

Notice that we have not used any initial conditions yet. We used the boundary conditions we were given ($u(0,t)=u(l,t)=0$), so Equation 12.3.14 is valid regardless of initial conditions as long as the string is held fixed at both ends. As you may suspect, the values of a_n and b_n will be calculated from the initial conditions. However, notice that in order to describe the movement of the string at all times we will need to calculate an infinite number of a_n-values and and infinite number of b_n-values. This sounds pretty intimidating, but you will see how all the time you spent learning about Fourier series will finally pay off. Before we look into how to do that, let's take a look at the individual solutions listed in Equation 12.3.13.

Each $u_n(x,t)$ is called a normal mode. For example, for $n=1$, we have

$$u_1(x,t)=\sin\left(\frac{\pi}{l}x\right)\left[p_1\sin(\omega_1t)+q_1\cos(\omega_1t)\right]$$

which is called the fundamental mode, or first harmonic.

Notice that this function is the product of a function that depends only on x ($\sin\left(\frac{\pi}{l}x\right)$) and another function that depends only on t, i.e.,

$$\left[p_1\sin(\omega_1t)+q_1\cos(\omega_1t)\right].$$

The function on t simply changes the amplitude of the sine function on x:

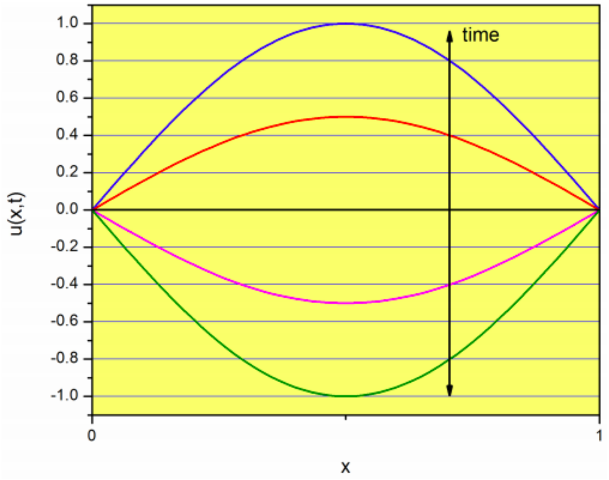


Figure 12.3.2: The fundamental mode or first harmonic. Different colors represent the string at different times. (CC BY-NC-SA; Marcia Levitus)

For $n = 2$, we have:

$$u_2(x,t) = \sin\left(2\frac{\pi}{l}x\right)\left[p_2 \sin(\omega_2 t) + q_2 \cos(\omega_2 t)\right]$$

which is called the first overtone, or second harmonic. Again, this function is the product of one function that depends on x only ($\sin\left(2\frac{\pi}{l}x\right)$), and another one that depends on t and changes the amplitude of $\sin\left(2\frac{\pi}{l}x\right)$ without changing its overall shape:

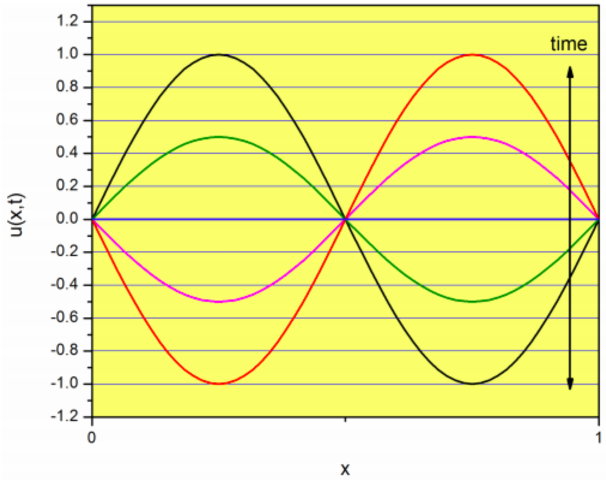


Figure 12.3.3: The first overtone or second harmonic. Different times are plotted in different colors (CC BY-NC-SA; Marcia Levitus)

For $n = 3$, we have:

$$u_3(x,t) = \sin\left(3\frac{\pi}{l}x\right)\left[p_3 \sin(\omega_3 t) + q_3 \cos(\omega_3 t)\right]$$

which is called the second overtone, or third harmonic. Again, this function is the product of one function that depends on x only ($\sin\left(3\frac{\pi}{l}x\right)$), and another one that depends on t and changes the amplitude of $\sin\left(3\frac{\pi}{l}x\right)$ without changing its overall shape:

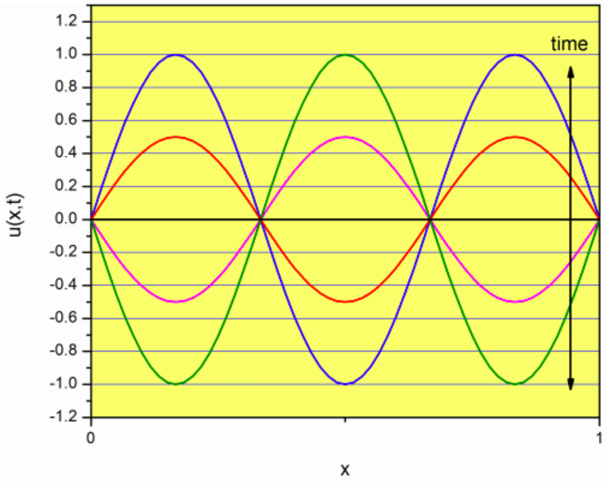


Figure 12.3.4: The second overtone or third harmonic. Different times are plotted in different colors (CC BY-NC-SA; Marcia Levitus)

If the initial shape of the string (i.e. the function $u(x,t)$ at time zero) is $\sin\left(\frac{\pi}{l}x\right)$ (Figure $12.3.2$, then the string will vibrate as shown in the figure, just changing the amplitude but not the overall shape. In more general terms, if $u(x,0)$ is one of the normal modes, the string will vibrate according to that normal mode, without mixing with the rest. However, in general, the shape of the string will be described by a linear combination of normal modes (Equation 12.3.14). If you recall from Chapter 7, a Fourier series tells you how to express a function as a linear combination of sines and cosines. The idea here is the same: we will express an arbitrary shape as a linear combination of normal modes, which are a collection of sine functions.

In order to do that, we need information about the initial shape: $u(x,0)$. We also need information about the initial velocity of all the points in the string: $\frac{\partial u(x,0)}{\partial t}$. The initial shape is the displacement of all points at time zero, and it is a function of x. Let's call this function $y_1(x)$:

$$u(x,0)=y_1(x) \tag{12.3.15}$$

The initial velocity of all points is also a function of x, and we will call it $y_2(x)$:

$$\frac{\partial u(x,0)}{\partial t}=y_2(x) \tag{12.3.16}$$

Both functions together represent the initial conditions, and be will used to calculate all the a_n and b_n coefficients. To simplify the problem, let's assume that at time zero we hold the string still, so the velocity of all points is zero:

$$\frac{\partial u(x,0)}{\partial t}=0$$

Let's see how we can use this information to finish the problem (i.e. calculate the coefficients a_n and b_n). From Equations 12.3.14 and 12.3.15:

$$u(x,t)=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)\left[a_n\sin(\omega_n t)+b_n\cos(\omega_n t)\right]$$

and applying the first initial condition:

$$u(x,0)=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)[b_n]=y_1(x) \tag{12.3.17}$$

This equation tells us that the initial shape, $y_1(x)$, can be described as an infinite sum of sine functions....sounds familiar? In Chapter 7, we saw that we can represent a periodic odd function $f(x)$ of period $2L$ as an infinite sum of sine functions (Equation $7.2.1$, $f(x)=\frac{a_0}{2}+\sum_{n=1}^{\infty}a_n\cos\left(\frac{n\pi x}{L}\right)+\sum_{n=1}^{\infty}b_n\sin\left(\frac{n\pi x}{L}\right)$):

$$f(x)=\sum_{n=1}^{\infty} b_n sin\left(\frac{n\pi x}{L}\right) \tag{12.3.18}$$

Comparing Equations 12.3.17 and 12.3.18, we see that in order to calculate the b_n coefficients of Equation 12.3.14, we need to create an odd extension of y_1 with period $2l$.

Let’s see how this works with an example. Let’s assume that the initial displacement is given by the function shown in the figure:

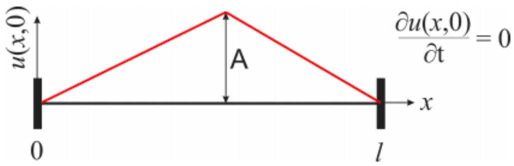


Figure 12.3.5: Initial conditions for the vibrating string problem (Equations 12.3.15 and 12.3.16). (CC BY-NC-SA; Marcia Levitus)

Equation 12.3.17 tells us that the function of Figure 12.3.5 can be expressed as an infinite sum of sine functions. If we figure out which sum, we will have the coefficients b_n we need to write down the expression of $u(x,y)$ we are seeking (Equation 12.3.14). We will still need the coefficients a_n, which will be calculated from the second initial condition (Equation 12.3.16).

Because we know the infinite sum of Equation 12.3.17 describes an odd periodic function of period $2l$, our first step is to extend $y_1(x)$ in an odd fashion:

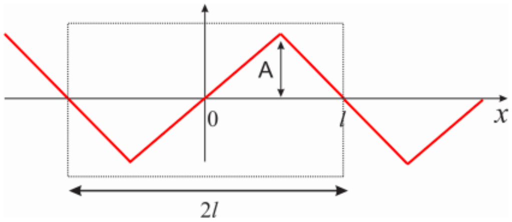


Figure 12.3.6: The odd extension of $y_1(x)$ (Figure 12.3.5). (CC BY-NC-SA; Marcia Levitus)

What is the Fourier series of the periodic function of Figure 12.3.6? Using the methods we learned in Chapter 7, we obtain:

$$y_1(x)=\frac{8A}{\pi^2}\left[\sin\frac{\pi x}{l}-\frac{1}{3^2}\sin\frac{3\pi x}{l}+\frac{1}{5^2}\sin\frac{5\pi x}{l}\ldots\right]=\frac{8A}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^2}\sin\left(\frac{(2n+1)\pi}{l}x\right) \tag{12.3.19}$$

From Equation 12.3.17

$u(x,0)=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)[b_n]=y_1(x)$

comparing Equations 12.3.17 and 12.3.19:

$$b_n=\begin{cases}0 & n=2,4,6\ldots\\ \dfrac{8A}{\pi^2n^2} & n=1,5,9\ldots\\ -\dfrac{8A}{\pi^2n^2} & n=3,7,11\ldots\end{cases} \tag{12.3.20}$$

Great! we have all the coefficients b_n, so we are just one step away from our final goal of expressing $u(x,t)$. Our last step is to calculate the coefficients a_n. We will use the last initial condition: $\frac{\partial u(x,0)}{\partial t}=y_2(x)$. Taking the partial derivative of Equation 12.3.14:

$$u(x,t)=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)[a_n\sin(\omega_n t)+b_n\cos(\omega_n t)]$$

$$\frac{\partial u(x,t)}{\partial t}=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)[a_n\omega_n\cos(\omega_n t)-b_n\omega_n\sin(\omega_n t)]$$

$$\frac{\partial u(x,0)}{\partial t}=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)\left[a_n\omega_n\right]=y_2(x) \tag{12.3.21}$$

Equation 12.3.21tells us that the function $y_2(x)$ can be expressed as an infinite sum of sine functions. Again, we need to create an odd extension of $y_2(x)$ and obtain its Fourier series: $y_2(x)=\sum_{n=1}^{\infty} b_n sin\left(\frac{n\pi x}{L}\right)$. The coefficients b_n of the Fourier series equal $a_n\omega_n$ (Equation 12.3.21). In this particular case:

$$\frac{\partial u(x,0)}{\partial t}=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)\left[a_n\omega_n\right]=0\rightarrow a_n=0$$

The coefficients a_n are zero, because the derivative needs to be zero for all values of x.

Now that we have all coefficients b_n and a_n we are ready to wrap this up. From Equations 12.3.14and 12.3.20:

$$u(x,t)=\sum_{n=1}^{\infty}\sin\left(\frac{n\pi}{l}x\right)\left[a_n\sin(\omega_n t)+b_n\cos(\omega_n t)\right] \tag{12.3.22}$$

$$=b_1\sin\left(\frac{\pi}{l}x\right)\cos(\omega_1 t)+b_3\sin\left(\frac{3\pi}{l}x\right)\cos(\omega_3 t)+b_5\sin\left(\frac{5\pi}{l}x\right)\cos(\omega_5 t)\ldots \tag{12.3.23}$$

$$=\frac{8A}{\pi^2}\left[\sin\left(\frac{\pi}{l}x\right)\cos(\omega_1 t)-\frac{1}{3^2}\sin\left(\frac{3\pi}{l}x\right)\cos(\omega_3 t)+\frac{1}{5^2}\sin\left(\frac{5\pi}{l}x\right)\cos(\omega_5 t)\ldots\right] \tag{12.3.24}$$

Recalling that $\omega_n=\frac{n\pi}{l}v$:

$$u(x,t)=\frac{8A}{\pi^2}\left[\sin\left(\frac{\pi}{l}x\right)\cos\left(\frac{\pi}{l}vt\right)-\frac{1}{3^2}\sin\left(\frac{3\pi}{l}x\right)\cos\left(\frac{3\pi}{l}vt\right)+\frac{1}{5^2}\sin\left(\frac{5\pi}{l}x\right)\cos\left(\frac{5\pi}{l}vt\right)\ldots\right]$$

$$u(x,t)=\frac{8A}{\pi^2}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^2}\sin\left(\frac{(2n+1)\pi}{l}x\right)\cos\left(\frac{(2n+1)\pi}{l}vt\right) \tag{12.3.25}$$

Success! We got a full description of the movement of the string. We just need to know the length of the string (l), the initial displacement of the midpoint (A) and the parameter v, and we can start plotting the shape of the string at different times. Just remember that *Mathematica* cannot plot a function defined as an infinite sum, so you will have to plot a truncated version of Equation 12.3.25. As usual, the more terms you include the better the approximation, but the longer the computer will take to execute the command. To see an amazing slow motion movie of a real string follow this youtube link.

The parameter v has units of length over time (e.g. m/s), and it depends on factors such as the material of the string, its tension, and its thickness. A string instrument like a guitar, for instance, has strings made of different materials, and held at different tensions. When plucked, they produce vibrations of different frequencies, which we perceive as different musical notes. In general, the vibration of the string will be a linear combination of the normal modes we talked about earlier in this section. Each normal mode has a unique frequency ($\omega_n = \frac{n\pi}{l}v$), and if this frequency is within our audible range, we will perceive it as a pure musical note. A linear combination of normal modes contains many frequencies, and we perceive them as a more complex sound.

Music is nice, but what about the applications of normal modes in chemistry? We already mentioned molecular vibrations in different chapters, and we know that the atoms in molecules are continuously vibrating following approximately harmonic motions. The same way that the vibration of the string of Figure $12.3.5$ can be expressed as a linear combination of all the normal modes (Figures $12.3.2$-$12.3.4$, we can express the vibrations of a polyatomic molecule as a linear combination of normal modes. As you will see in your advanced physical chemistry courses, a non-linear polyatomic molecule has $3n-6$ vibrational normal modes, where n is the number of atoms. For the molecule of water, for example, we have 3 normal modes:

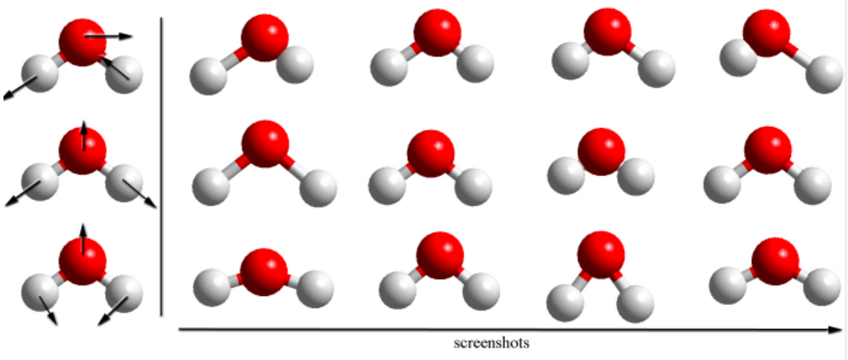


Figure $12.3.7$: The normal modes of vibration of water (CC BY-NC-SA; Marcia Levitus)

Any other type of vibration can be expressed as a linear combination of these three normal modes. As you can imagine, these motions occur very fast. Typically, you may see of the order of 10^{12} vibrations per second. The most direct way of probing the vibrations of a molecule is through infra-red spectroscopy, and in fact you will measure and analyze the vibrational spectra of simple molecules in your 300-level physical chemistry labs.

12.4: Molecular Diffusion

Molecular diffusion is the thermal motion of molecules at temperatures above absolute zero. The rate of this movement is a function of temperature, viscosity of the fluid and the size and shape of the particles. Diffusion explains the net flux of molecules from a region of higher concentration to one of lower concentration. The term "diffusion" is also generally used to describe the flux of other physical quantities. For instance, the diffusion of thermal energy (heat) is described by the heat equation, which is mathematically identical to the diffusion equation we'll consider in this section.

To visualize what we mean by molecular diffusion, consider a red dye diffusing in a test tube. Suppose the experiment starts by placing a sample of the dye in a thin layer half way down the tube. Diffusion occurs because all molecules move due to their thermal energy. Each molecule moves in a random direction, meaning that if you wait long enough, molecules will end up being randomly distributed throughout the tube. This means that there is a net movement of dye molecules from areas of high concentration (the central band) into areas of low concentration (Figure $12.4.1$ The rate of diffusion depends on temperature, the size and shape of the molecules, and the viscosity of the solvent.

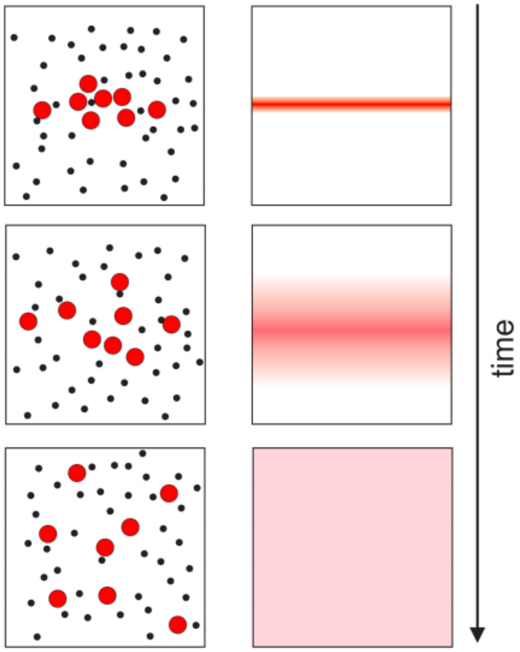


Figure 12.4.1: Molecular diffusion. A microscopic picture of diffusion is shown on the left, and a macroscopic view is pictured on the right. The red circles represent the solute molecules, which move randomly due to their thermal energy. (CC BY-NC-SA; Marcia Levitus)

The diffusion equation that describes how the concentration of solute (in this case the red dye) changes with position and time is:

$$\nabla^2 C(\mathbf{r},t) = \frac{1}{D}\frac{\partial C(\mathbf{r},t)}{\partial t} \tag{12.4.1}$$

where $\mathbf{r}$ is a vector representing the position in a particular coordinate system. This equation is known as Fick's second law of diffusion, and its solution depends on the dimensionality of the problem (1D, 2D, 3D), and the initial and boundary conditions. If molecules are able to move in one dimension only (for example in a tube that is much longer than its diameter):

$$\frac{\partial^2 C(x,t)}{\partial x^2} = \frac{1}{D}\frac{\partial C(x,t)}{\partial t} \tag{12.4.2}$$

Let's assume that the tube has a length L and it is closed at both ends. Mathematically, this means that the flux of molecules at $x=0$ and $x=L$ is zero. The flux is defined as the number of moles of substance that cross a $1m^2$ area per second, and it is mathematically defined as

$$J = -D\frac{\partial C(x,t)}{\partial x} \tag{12.4.3}$$

If the tube is closed, molecules at $x=0$ cannot move from the right side to the left side, and molecules at $x=L$ cannot move from the left side to the right side. Mathematically:

$$\frac{\partial C(0,t)}{\partial x}=\frac{\partial C(L,t)}{\partial x}=0 \tag{12.4.4}$$

These will be the boundary conditions we will use to solve the problem We still need an initial condition, which in this case it is the initial concentration profile: $C(x,0)=y(x)$. Notice that because of mass conservation, the integral of $C(x)$ should be constant at all times. We will not use this to solve the problem, but we can verify that the solution satisfies this requirement.

Regardless of initial conditions, the concentration profile will be expressed as (Problem 12.3):

$$C(x,t)=\sum_{n=0}^{\infty} a_n \cos\left(\frac{n\pi}{L}x\right) e^{-\left(\frac{n\pi}{L}\right)^2 Dt} \tag{12.4.5}$$

In order to calculate the coefficients a_n, we need information about the initial concentration profile: $C(x,0)=y(x)$.

$$C(x,0)=\sum_{n=0}^{\infty} a_n \cos\left(\frac{n\pi}{L}x\right)=y(x) \tag{12.4.6}$$

This expression tells us that the function $y(x)$ can be expressed as an infinite sum of cosines. We know from Chapter 7 that an infinite sum of cosines like this represents an even periodic function of period $2L$, so in order to find the coefficients a_n, we need to construct the even periodic extension of the function $y(x)$ and find its Fourier series. For example, assume that the initial concentration profile is given by Figure $12.4.2$. Imagine that you have water in the right half-side of the tube, and a 1M solution of red dye on the left half-side. At time zero, you remove the barrier that separates the two halves, and watch the concentration evolve as a function of time. Before we calculate these concentration profiles, let's think about what we expect at very long times, when the dye is allowed to fully mix with the water. We know that the same number of molecules present initially need to be re-distributed in the full length of the tube, so the concentration profile needs to be constant at 0.5M. It is a good idea that you sketch what you imagine happens in between before going through the math and seeing the results.

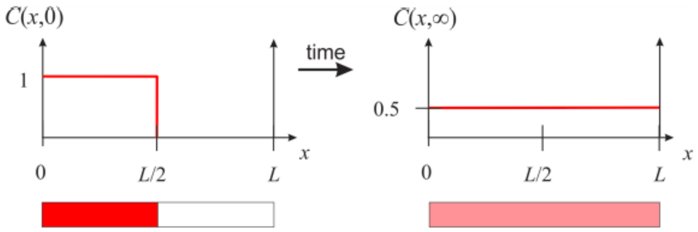


Figure 12.4.2: The initial and final concentration profiles, $C(x,0)$ and $C(x,\infty)$. The diagrams at the bottom represent a cartoon of what the tube would look like at time zero and at time infinity (CC BY-NC-SA; Marcia Levitus)

In order to calculate the coefficients a_n that we need to complete Equation $12.4.5$, we need to express $C(x,0)$ as an infinite sum of cosine functions, and therefore we need the even extension of the function:

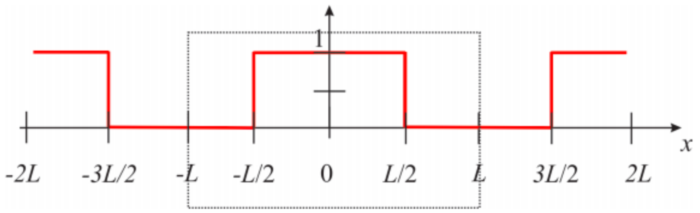


Figure 12.4.3: The even extension of the function $C(x,0)$ (CC BY-NC-SA; Marcia Levitus)

Let's calculate the Fourier series of this periodic function of period $2L$ (Equation 7.2.1, $f(x)=\frac{a_0}{2}+\sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right)+\sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right)$).

$$f(x)=\frac{a_0}{2}+\sum_{n=1}^{\infty} a_n cos\left(\frac{n\pi x}{L}\right)$$

$$a_0 = \frac{1}{L}\int_{-L}^{L} f(x)dx$$

$$a_n = \frac{1}{L}\int_{-L}^{L} f(x)\cos\left(\frac{n\pi x}{L}\right)dx$$

Let’s assume $L = 1cm$ (we will use D in units of cm^2/s and t in seconds):

$$a_0 = \frac{1}{L}\int_{-L}^{L} f(x)dx = \int_{-1/2}^{1/2} 1dx = 1$$

$$a_n = \int_{-1/2}^{1/2} 1\cos(n\pi x)dx = \frac{1}{n\pi}\sin(n\pi x)\,|_{-1/2}^{1/2} = \frac{1}{n\pi}[\sin(n\pi/2) - \sin(-n\pi/2)]$$

because $\sin x$ is odd:

$$a_n = \frac{2}{n\pi}\sin(n\pi/2) \to a_1 = \frac{2}{\pi}, a_2 = 0, a_3 = -\frac{2}{3\pi}, a_4 = 0, a_5 = \frac{2}{5\pi}\ldots$$

and therefore:

$$C(x,0) = \frac{1}{2} + \frac{2}{\pi}\sum_{n=0}^{\infty}(-1)^n\frac{1}{2n+1}\cos[(2n+1)\pi x]$$

and the complete description of $C(x,t)$ is (Equation 12.4.5):

$$C(x,t) = \frac{1}{2} + \frac{2}{\pi}\sum_{n=0}^{\infty}(-1)^n\frac{1}{2n+1}\cos[(2n+1)\pi x]e^{-[(2n+1)\pi]^2Dt} \tag{12.4.7}$$

Let’s plot $C(x,t)$ at different times assuming $L = 1cm$ and $D = 6.5\times10^{-6}cm^2s^{-1}$, which is the diffusion coefficient of sucrose (regular sugar) in water.

Notice that the derivative $\frac{\partial C(x,t)}{\partial x}$ is zero at both $x = 0$ and $x = L = 1cm$ at all times, as it should be the case given the boundary conditions. Also, the area under the curve is constant due to mass conservation. In addition notice how long it takes for diffusion to mix the two halves of the tube! It would take about a day for the concentration to be relatively homogeneous in a 1-cm tube, which explains why it is a good idea to stir the sugar in your coffee with a spoon instead of waiting for diffusion to do the job. Diffusion is inefficient because molecules move in random directions, and each time they bump into a molecule of water they change their direction. Imagine that you need to walk from the corner of Apache and Rural to the corner of College and University Ave, and every time you make a step you throw a four-sided die to decide whether to move south, north, east or west. You might eventually get to your destination, but it will likely take you a long time.

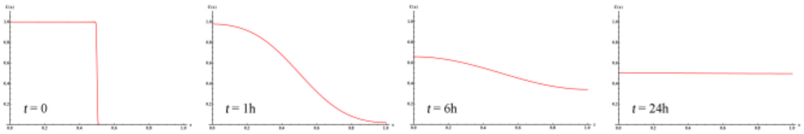


Figure 12.4.4: Concentration profile at time 0, 1 min, 6 h and 1 day (CC BY-NC-SA; Marcia Levitus)

12.5: Problems

Problem 12.5.1

Find $f(x,y)$. Note: In order to obtain all possible solutions in each case you will have to consider that the separation constant can be positive, negative, or zero.

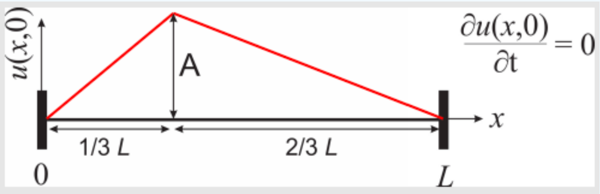
1. $2\frac{\partial f}{\partial x}+\frac{\partial f}{\partial y}=0$
2. $y\frac{\partial f}{\partial x}-x\frac{\partial f}{\partial y}=0$
3. $\frac{\partial^2 f}{\partial x^2}+\frac{\partial^2 f}{\partial y^2}=0$

Problem 12.5.2

Consider a uniform string under tension and of length L. At time $t=0$ the string is displaced as shown in the figure and released. The displacement of the string from its horizontal position $(u(x,t))$ depends on both x and t and satisfies the following PDE:

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

where v is a constant that depends on the characteristics of the string.



1. Obtain an expression for $u(x,t)$. Note that most of the problem is solved in the book, but you still need to show ALL steps.
2. In the lab: Assume $v=440\text{m/s},\ A=5\text{cm}$ and $L=12\text{cm}$. Create a function $u(x,t)$ with the result of 1). Remember that you can't plot an infinite sum, so you will have to truncate it when plotting in *Mathematica*. Use the function "Manipulate" to generate an animation of the vibrating string. Be sure you run it slowly so you can see the motion).

Problem 12.5.3

Use the separation of variables method to obtain an expression for $C(x,t)$ for the system described in Section 12.4:

$$\frac{\partial^2 C(x,t)}{\partial x^2}=\frac{1}{D}\frac{\partial C(x,t)}{\partial t}$$

$$\frac{\partial C(0,t)}{\partial x}=\frac{\partial C(L,t)}{\partial x}=0$$

The solution is:

$$C(x,t)=\sum_{n=0}^{\infty}a_n\cos\left(\frac{n\pi}{L}x\right)e^{-\left(\frac{n\pi}{L}\right)^2 Dt}$$

where the coefficients a_n depend on the initial concentration profile (initial conditions).

Problem 12.5.4

Continue the previous problem and obtain the full expression of $C(x,t)$ using the initial condition shown in Figure $12.5.1$:

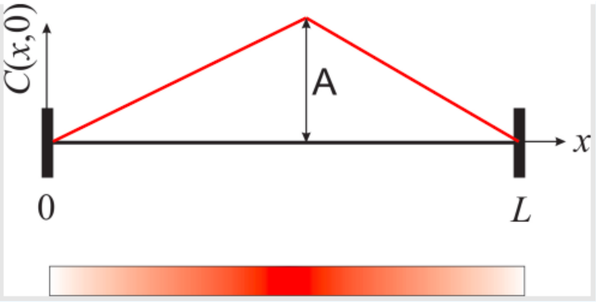


Figure $12.5.1$: The initial concentration profile, $C(x,0)$. The diagram at the bottom represents a cartoon of what the tube would look like at time zero, with higher concentration of red dye at the center and zero concentration at both ends.

The even extension of this function is (compare with Figure $12.3.6$)

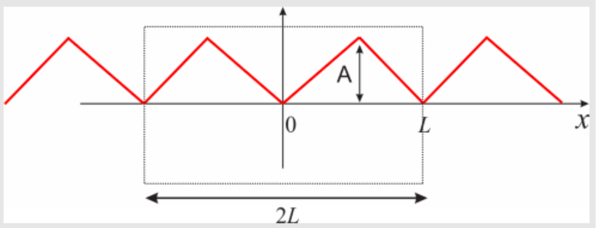


Figure $12.5.2$: The even extension of y(x) (Figure $12.5.1$).

In the lab:

- Assume $L = 1\text{cm}, \ A = 1\text{M}$, and $D = 6.510 - 10\text{m}^2/\text{s}$ (the diffusion coefficient of glucose in water) Use Manipulate to create a movie that shows how $C(x)$ changes with time.
- Plot $C(0,t)$ (that is, the concentration at the end of the tube as a function of time). How long does it take until the concentration reaches 0.1M? (give an approximate value). This should demonstrate the need of stirring your coffee after adding sugar (i.e. waiting until sugar diffuses on its own would take too long for you to enjoy a hot cup of coffee).
- Repeat the previous question assuming $L = 1\mu\text{m}$ (the order of magnitude of the diameter of the nucleus of a cell). This should demonstrate that diffusion is an efficient mechanism for molecular transport inside small cells like bacteria, or inside the nucleus of larger cells.

CHAPTER OVERVIEW

13: Determinants

Chapter Objectives

- Learn how to calculate the determinant of a square matrix.
- Understand how to solve systems of simultaneous linear equations using determinants.
- Learn the properties of determinants.

13.1: The Solutions of Simultaneous Linear Equations

The concept of determinants has its origin in the solution of simultaneous linear equations. In physical chemistry, they are an important tool in quantum mechanics

Suppose you want to solve the following system of two equations with two unknowns (x and y):

$$a_1x+b_1y=c_1$$

$$a_2x+b_2y=c_2$$

In order to find y, we could use the following general procedure: we multiply the first equation by a_2 and the second by a_1, and subtract one line from the other to cancel the term in x:

$$a_1x+b_1y=c_1 \overset{\times a_2}{\rightarrow} a_1a_2x+b_1a_2y=c_1a_2$$

$$a_2x+b_2y=c_2 \overset{\times a_1}{\rightarrow} a_1a_2x+b_2a_1y=c_2a_1$$

$$\left.\begin{array}{l} a_1a_2x+b_1a_2y=c_1a_2 \\ a_1a_2x+b_2a_1y=c_2a_1 \end{array}\right\} \rightarrow (b_2a_1-b_1a_2)y=a_1c_2-a_2c_1 \rightarrow y=\frac{a_1c_2-a_2c_1}{b_2a_1-b_1a_2}$$

We can follow the same strategy to find x: we multiply the first equation by b_2 and the second by b_1, and subtract one line from the other to cancel the term in y:

$$a_1x+b_1y=c_1 \overset{\times b_2}{\rightarrow} a_1b_2x+b_1b_2y=c_1b_2$$

$$a_2x+b_2y=c_2 \overset{\times b_1}{\rightarrow} b_1a_2x+b_2b_1y=c_2b_1$$

$$\left.\begin{array}{l} a_1b_2x+b_1b_2y=c_1b_2 \\ b_1a_2x+b_2b_1y=c_2b_1 \end{array}\right\} \rightarrow (b_2a_1-b_1a_2)x=b_2c_1-b_1c_2 \rightarrow x=\frac{b_2c_1-b_1c_2}{b_2a_1-b_1a_2}$$

We define a 2×2 determinant as:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad-cb$$

The determinant, which is denoted with two parallel bars, is a number. For example,

$$\begin{vmatrix} 3 & -1 \\ 1/2 & 2 \end{vmatrix} = 3\times 2-(-1)\times 1/2=13/2$$

Let’s look at the expressions we obtained for x and y, and write them in terms of determinants:

$$x=\frac{b_2c_1-b_1c_2}{b_2a_1-b_1a_2}=\frac{\begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

$$y=\frac{a_1c_2-a_2c_1}{b_2a_1-b_1a_2}=\frac{\begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}$$

Let’s look at our equations, and see how these determinants are constructed from the coefficients.

$$a_1x+b_1y=c_1$$

$$a_2x+b_2y=c_2$$

The determinant in the denominator of both x and y is the determinant of the coefficients on the left-side of the equal sign:

$$\left.\begin{array}{l} a_1x+b_1y=c_1 \\ a_2x+b_2y=c_2 \end{array}\right\} \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}$$

The numerator in the expression of y is built by replacing the coefficients in the y-column with the coefficients on the right side of the equation:

$$\left.\begin{array}{l} a_1x+b_1y=c_1 \\ a_2x+b_2y=c_2 \end{array}\right\} \begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}$$

The numerator in the expression of x is built by replacing the coefficients in the x-column with the coefficients on the right side of the equation:

$$\left.\begin{array}{l} a_1x+b_1y=c_1 \\ a_2x+b_2y=c_2 \end{array}\right\} \begin{vmatrix} c_1 & b_1 \\ c_2 & b_2 \end{vmatrix}$$

We can extend this idea to n equations with n unknowns $(x_1, x_2, x_3, \ldots, x_n)$.

$$\begin{array}{ccccccccc} a_{11}x_1 & + & a_{12}x_2 & + & \cdots & + & a_{1n}x_n & =b_1 \\ a_{21}x_1 & + & a_{22}c_2 & + & \cdots & + & a_{2n}x_n & =b_2 \\ \vdots & & \vdots & & \ddots & & \vdots & \vdots \\ a_{n1}x_1 & + & a_{n2}c_2 & + & \cdots & + & a_{nn}x_n & =b_n \end{array}$$

Note that we use two subscripts to identify the coefficients. The first refers to the row, and the second to the column. Let's define the determinant D as the determinant of the coefficients of the equation (the ones on the left side of the equal sign):

$$D=\begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix}$$

and let's define the determinant D_k as the one obtained from D by replacement of the kth column of D by the column with elements $b_1, b_2 \ldots b_n$. For example, D_2 is

$$D_2=\begin{vmatrix} a_{11} & b_1 & \cdots & a_{1n} \\ a_{21} & b_2 & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & b_n & \cdots & a_{nn} \end{vmatrix}$$

The unknowns of the system of equations are calculated as:

$$x_1=\frac{D_1}{D}, x_2=\frac{D_2}{D}, \ldots, x_n=\frac{D_n}{D}$$

For example, let's say we want to find x, y and z in the following system of equations:

$$2x+3y+8z=0$$

$$x-\frac{1}{2}y-3z=\frac{1}{2}$$

$$-x-y-z=\frac{1}{2}$$

We can calculate the unknowns as;

$$x=\frac{D_1}{D}, y=\frac{D_2}{D}, z=\frac{D_3}{D}$$

where

$$D = \begin{vmatrix} 2 & 3 & 8 \\ 1 & -1/2 & -3 \\ -1 & -1 & -1 \end{vmatrix}$$

$$D_1 = \begin{vmatrix} 0 & 3 & 8 \\ 1/2 & -1/2 & -3 \\ 1/2 & -1 & -1 \end{vmatrix}$$

$$D_2 = \begin{vmatrix} 2 & 0 & 8 \\ 1 & 1/2 & -3 \\ -1 & 1/2 & -1 \end{vmatrix}$$

$$D_3 = \begin{vmatrix} 2 & 3 & 0 \\ 1 & -1/2 & 1/2 \\ -1 & -1 & 1/2 \end{vmatrix}$$

In order to do this, we need to learn how to solve 3×3 determinants, or in general, $n \times n$ determinants.

13.2: Calculation of a 3 × 3 determinant

There are several techniques to calculate determinants, but if this topic is new to you, expanding along the first row is the easiest (although maybe not the most computationally efficient) way of doing it.

A 3 $\times$ 3 matrix is calculated as:

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = a_{11}\begin{vmatrix} a_{22} & a_{23} \\ a_{32} & a_{33} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} \\ a_{31} & a_{33} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} \\ a_{31} & a_{32} \end{vmatrix} \tag{13.2.1}$$

Notice that we multiply each entry in the first row by the determinant formed by what is left after deleting the corresponding row and column. In addition, notice that we alternate signs. Formally, the sign that corresponds to a particular entry a_{ij} is $(-1)^{i+j}$, but if we use the first raw we will always start with a "+" and alternate signs afterwards. A schematics of the procedure is shown in Figure 13.2.1.

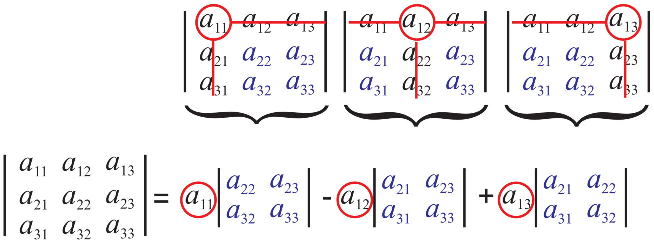


Figure 13.2.1: A 3×3 determinant (CC BY-NC-SA; Marcia Levitus)

We can use the same idea to calculate a determinant of any size. For example, for a 4×4 determinant:

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} = a_{11}\begin{vmatrix} a_{22} & a_{23} & a_{24} \\ a_{32} & a_{33} & a_{34} \\ a_{42} & a_{43} & a_{44} \end{vmatrix} - a_{12}\begin{vmatrix} a_{21} & a_{23} & a_{24} \\ a_{31} & a_{33} & a_{34} \\ a_{41} & a_{43} & a_{44} \end{vmatrix} + a_{13}\begin{vmatrix} a_{21} & a_{22} & a_{24} \\ a_{31} & a_{32} & a_{34} \\ a_{41} & a_{42} & a_{44} \end{vmatrix} - a_{14}\begin{vmatrix} a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \\ a_{41} & a_{42} & a_{43} \end{vmatrix} \tag{13.2.2}$$

The 3×3 determinants are then calculated using Equation 13.2.1.

Example 13.2.1

Find x in the following system of equations:

$$\begin{aligned} 2x + 3y + 8z &= 0 \\ x - \frac{1}{2}y - 3z &= \frac{1}{2} \\ -x - y - z &= \frac{1}{2} \end{aligned}$$

Solution

We can calculate the x as;

$$x = \frac{D_1}{D}$$

where

$$D = \begin{vmatrix} 2 & 3 & 8 \\ 1 & -1/2 & -3 \\ -1 & -1 & -1 \end{vmatrix}$$

and

$$D_1 = \begin{vmatrix} 0 & 3 & 8 \\ 1/2 & -1/2 & -3 \\ 1/2 & -1 & -1 \end{vmatrix}$$

D is a 3x3 determinant D and can be expanded using quation 13.2.1:

$$\begin{aligned} D &= 2\begin{vmatrix} -1/2 & -3 \\ -1 & -1 \end{vmatrix} - 3\begin{vmatrix} 1 & -3 \\ -1 & -1 \end{vmatrix} + 8\begin{vmatrix} 1 & -1/2 \\ -1 & -1 \end{vmatrix} \\ &= 2\times(-5/2)-(3)\times(-4)+8\times(-3/2)=-5 \end{aligned}$$

The determinant D_1 is similarly expanded:

$$\begin{aligned} D_1 &= 0\begin{vmatrix} -1/2 & -3 \\ -1 & -1 \end{vmatrix} - 3\begin{vmatrix} 1/2 & -3 \\ 1/2 & -1 \end{vmatrix} + 8\begin{vmatrix} 1/2 & -1/2 \\ 1/2 & -1 \end{vmatrix} \\ &= 0\times(-5/2)-(3)\times(1)+8\times(-1/4)=-5 \end{aligned}$$

So,

$$x=\frac{D_1}{D}=1$$

To practice, finish this problem and obtain y and z (Problem 13.1).

✓ Example 13.2.2

Show that a 3×3 determinant that contains zeros below the principal diagonal (top left to bottom right) is the product of the diagonal elements.

Solution

We are asked to prove that

$$D=\begin{vmatrix} a & b & c \\ 0 & d & e \\ 0 & 0 & f \end{vmatrix}=adf$$

Because we have two zeros in the first column, it makes more sense to calculate the determinant by expanding along the first column instead of the first row. Yet, if you feel uncomfortable doing this at this point we can expand along the first row as we just learned:

$$D=a\times\begin{vmatrix} d & e \\ 0 & f \end{vmatrix}-b\times\begin{vmatrix} 0 & e \\ 0 & f \end{vmatrix}+c\times\begin{vmatrix} 0 & d \\ 0 & 0 \end{vmatrix}=a\times d\times f$$

The conclusion is true in any dimension.

Need help? The links below contain solved examples. The determinant of a 3x3 matrix: http://tinyurl.com/n2a3uxw

External links:

- Finding the determinant of a 3x3 matrix: http://patrickjmt.com/finding-the-determinant-of-a-3-x-3-matrix/
- Solving a system of 3 linear equations: http://patrickjmt.com/cramers-rule-to-solve-a-system-of-3-linear-equations-example-1/

13.3: The Determinant as a Volume

Before discussing the properties of determinants, it will be useful to note that a determinant represents the volume of a box.

In two dimensions, the absolute value of a 2×2 determinant represents the area of the parallelogram whose sides are the two columns (or rows) of the determinant. Suppose you have two vectors: $\vec{v_1} = (b, d)$ and $\vec{v_2} = (a, c)$ (see Figure $13.3.2$). The area of the parallelogram constructed with these two vectors as sides is the absolute value of the determinant whose columns are $\vec{v_1}$ and $\vec{v_2}$:

$$A = \begin{vmatrix} b & a \\ d & c \end{vmatrix}$$

A geometrical proof of this statement is shown in Figure $13.3.1$. The sign of the determinant is related to the orientation of the parallelogram. If you extend your right hand, and use your thumb and index finger to represent the two vectors, the determinant will be positive if the vector along your thumb is in the first column and the vector and your index finger is in the second column, and will be negative if it is the other way around (Figure $13.3.2$).

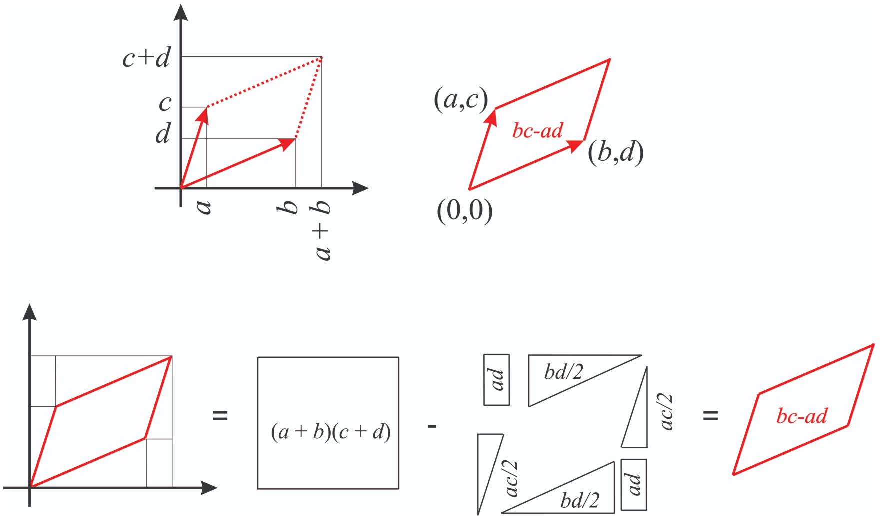


Figure $13.3.1$: A $2\times$ 2 determinant as the area of a parallelogram. The area of the parallelogram is calculated as the area of the rectangle of sides $(a+b)$ and $(c+d)$ minus the areas of the triangles and rectangles shown in the figure (CC BY-NC-SA; Marcia Levitus)

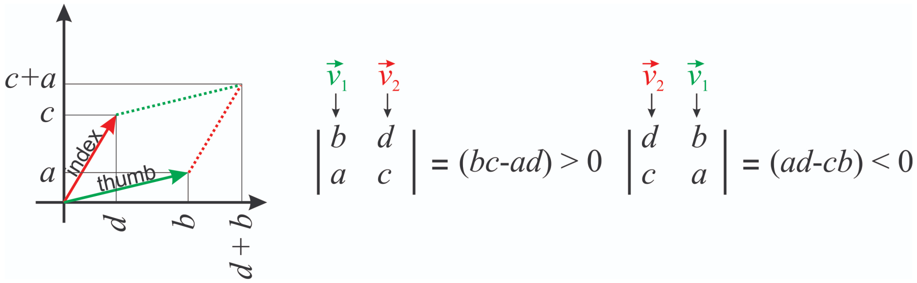


Figure $13.3.2$: The order of the vectors in the determinant determines the sign. (CC BY-NC-SA; Marcia Levitus)

For a 3×3 determinant, its absolute value represents the volume of the parallelepiped ("the box") whose edges are the vectors that are the columns of the determinant (Figure $13.3.3$)

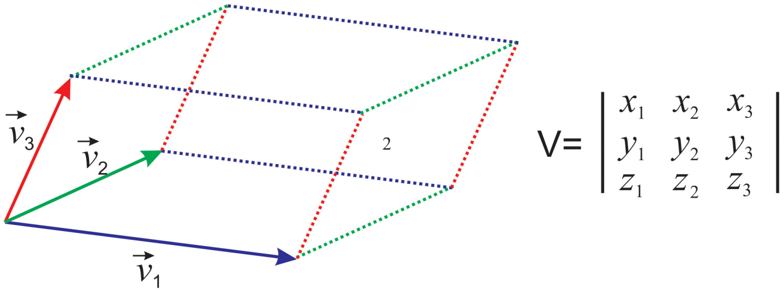


Figure 13.3.3: A 3× 3 determinant as the volume of a parallelepiped. (CC BY-NC-SA; Marcia Levitus)

This notion will help us understand and remember some useful properties of determinants. For example, we can readily conclude that a determinant that contains non-zero entries only in the main diagonal (top left to bottom right) is the product of the diagonal entries:

$$\begin{vmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{vmatrix} = abc$$

This is true because the columns represent vectors that are aligned with the x, y and z axes respectively, so the volume of the resulting box is the product of the dimensions along x, y and z (Figure $13.3.4$):

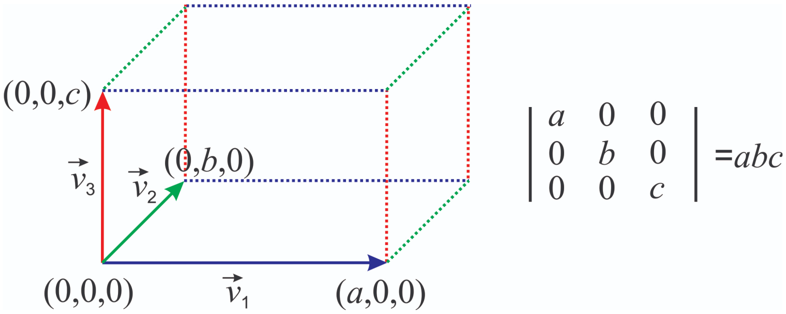


Figure 13.3.4: The determinant of a 3× 3 diagonal matrix (CC BY-NC-SA; Marcia Levitus)

13.4: Properties of Determinants

1-

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = 1 \tag{13.4.1}$$

This is true in any dimension, and can be understood easily from geometrical arguments. In two dimensions, the columns represent unitary vectors along the x and y axis, and the parallelogram is therefore a square of unit area. In three dimensions, the columns represent unitary vectors along the x, y and z axis, and the box is therefore a cube of unit volume.

2-

Antisymmetry: If two rows (or two columns) of a determinant are interchanged, the value of the determinant is multiplied by -1. This property is extremely useful in quantum mechanics, so it is worth remembering!

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = -\begin{vmatrix} b & a & c \\ e & d & f \\ h & g & i \end{vmatrix} = -\begin{vmatrix} d & e & f \\ a & b & c \\ g & h & i \end{vmatrix} \tag{13.4.2}$$

We already discussed this property in two dimensions (see Figure $13.3.3$).

3-

Scalars can be factored out from rows and columns.

$$\begin{vmatrix} a & b & c \\ \lambda d & \lambda e & \lambda f \\ g & h & i \end{vmatrix} = \lambda \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} \tag{13.4.3}$$

Geometrically speaking, if you multiply the length of one of the edges of the parallelepiped by λ, the volume is also multiplied by λ.

4-

Addition rule: If all the elements of any row (or column) are written as the sum of two terms, then the determinant can be written as the sum of two determinants

$$\begin{vmatrix} a+b & c & d \\ e+f & g & h \\ i+j & k & l \end{vmatrix} = \begin{vmatrix} a & c & d \\ e & g & h \\ i & k & l \end{vmatrix} + \begin{vmatrix} b & c & d \\ f & g & h \\ j & k & l \end{vmatrix} \tag{13.4.4}$$

$$\begin{vmatrix} a+b & c+d & e+f \\ g & h & i \\ j & k & l \end{vmatrix} = \begin{vmatrix} a & c & e \\ g & h & i \\ j & k & l \end{vmatrix} + \begin{vmatrix} b & d & f \\ g & h & i \\ j & k & l \end{vmatrix} \tag{13.4.5}$$

5-

The value of a determinant is zero if two rows or two columns are equal. This is a consequence of property 2. Exchanging the two identical rows is supposed to change the sign of the determinant, but we know that exchanging two identical rows does nothing to the determinant. Therefore, the determinant has to be zero.

Geometrically, two edges of the box would be the same, rendering a flat box with no volume.

$$\begin{vmatrix} {\color{red}a} & {\color{red}a} & {\color{blue}b} \\ {\color{red}c} & {\color{red}c} & {\color{blue}d} \\ {\color{red}e} & {\color{red}e} & {\color{blue}f} \end{vmatrix} = 0 \tag{13.4.6}$$

6-

The value of a determinant is unchanged if one row or column is added or subtracted to another. This property is a consequence of properties 4 and 5:

$$\begin{vmatrix} a+b & b & c \\ d+e & e & f \\ g+h & h & i \end{vmatrix} = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} + \begin{vmatrix} b & b & c \\ e & e & f \\ h & h & i \end{vmatrix} \tag{13.4.7}$$

7-

A special case of property 3 is that if all the elements of a row or column are zero, the value of the determinant is zero. In geometrical terms, if one of the edges is a point, the volume is zero.

$$\begin{vmatrix} a & b & c \\ 0 & 0 & 0 \\ d & e & f \end{vmatrix} = 0 \tag{13.4.8}$$

8-

The value of a determinant is zero if one row (or column) is a multiple of another row (or column). Geometrically, this means that two edges of the parallelepiped lie on the same line, and therefore the volume is zero. This is a consequence of properties 3 and 5:

$$\begin{vmatrix} a & b & c \\ \lambda a & \lambda b & \lambda c \\ d & e & f \end{vmatrix} = \lambda \begin{vmatrix} a & b & c \\ a & b & c \\ d & e & f \end{vmatrix} = 0 \tag{13.4.9}$$

9-

Transposition: the value of the determinant is unchanged if its rows and columns are interchanged. This property can be derived from the previous properties, although it is a little complicated for the level of this course.

$$\begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = \begin{vmatrix} a & d & g \\ b & e & h \\ c & f & i \end{vmatrix} \tag{13.4.10}$$

Geometrically, interchanging rows by columns rotates the parallelogram (or the box in 3D) without changing the area (or volume). Figure 13.4.1 shows that

$$\begin{vmatrix} b & a \\ d & c \end{vmatrix} = \begin{vmatrix} b & d \\ a & c \end{vmatrix}$$

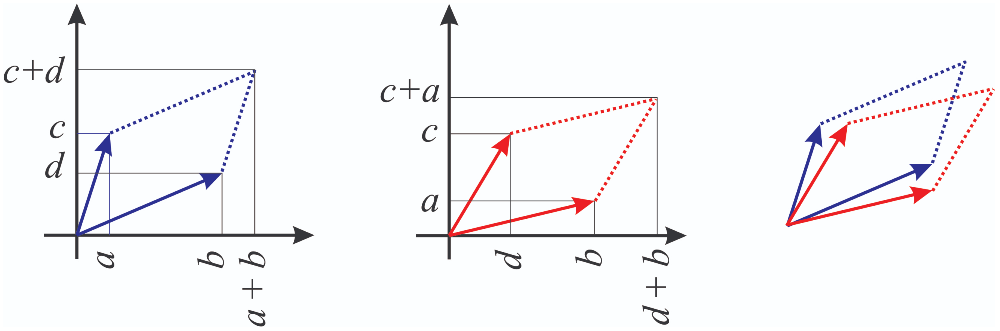


Figure 13.4.1: Transposing rows and columns rotates the parallelogram (CC BY-NC-SA; Marcia Levitus)

✓ Example 13.4.1

Determine the value of the following determinant by inspection.

$$\begin{vmatrix} 2 & 6 & 1 \\ -4 & 4 & -2 \\ 2 & -3 & 1 \end{vmatrix}$$

Solution

We notice that the third column is a multiple of the first:

$$\begin{aligned} \begin{vmatrix} 2 & 6 & 1 \\ -4 & 4 & -2 \\ 2 & -3 & 1 \end{vmatrix} = \begin{vmatrix} 1\times 2 & 6 & 1 \\ -2\times 2 & 4 & -2 \\ 1\times 2 & -3 & 1 \end{vmatrix} \\ = 2\times \begin{vmatrix} 1 & 6 & 1 \\ -2 & 4 & -2 \\ 1 & -3 & 1 \end{vmatrix} \\ = 0 \end{aligned}$$

The determinant is zero because two of its columns are the same.

13.5: Problems

Problem 13.5.1

Finish the problem of Example $13.1.1$ and obtain y and z.

Problem 13.5.2

Use determinants to solve the equations:

A)

$$\begin{aligned} x+y+z&=6\\ x+2y+3z&=14\\ x+4y+9z&=36 \end{aligned}$$

B)

$$\begin{aligned} x+iy-z&=0\\ ix+y+z&=0\\ x+2y-iz&=1 \end{aligned}$$

Problem 13.5.3

Show that a 3×3 determinant that contains zeros above the principal diagonal is the product of the diagonal elements.

$$D=\begin{vmatrix} a & 0 & 0\\ b & c & 0\\ d & e & f \end{vmatrix}=acf$$

Problem 13.5.4

Prove that

$$D=\begin{vmatrix} 1 & 2 & 3\\ 2 & 3 & 3\\ 3 & 4 & 3 \end{vmatrix}=0$$

using the properties of determinants (that is, without calculating the determinant!). Clearly state the properties you use in each step.

Exercise 13.5.5

In previous lectures, we discussed how to perform double and triple integrals in different coordinate systems. For instance, we learned that the area elements and volume elements are:

2D:

Cartesian: $dA=dx.\,dy$
Polar: $dA=r.\,dr.\,d\theta$

3D:

Cartesian: $dV=dx.\,dy.\,dz$
Spherical: $dV=r^2.\,\sin\theta dr.\,d\theta d\phi$

In general, for any coordinate system, we can express the area (or volume) element in a new coordinate system using the Jacobian (J). For example, in polar coordinates in two dimensions:

$$dA = dx.dy = J.dr.d\theta$$

where the Jacobian is defined as:

$$J = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} \end{vmatrix}$$

a) Calculate the Jacobian in two-dimensional polar coordinates and show that $dA = r.dr.d\theta$.

In spherical coordinates,

$$dV = dx.dy.dz = J.dr.d\theta.d\phi$$

where

$$J = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix}$$

b) Calculate the Jacobian in three-dimensional spherical coordinates and show that

$$dV = r^2.\sin\theta dr.d\theta d\phi$$

CHAPTER OVERVIEW

14: Vectors

Objectives

- Be able to perform operations with vectors: addition, subtraction, dot product, cross product.
- Understand how to calculate the modulus of a vector, including vectors containing complex entries.
- Understand how to normalize vectors.

14.1: Introduction to Vectors

In this chapter we will review a few concepts you probably know from your physics courses. This chapter does not intend to cover the topic in a comprehensive manner, but instead touch on a few concepts that you will use in your physical chemistry classes.

A vector is a quantity that has both a magnitude and a direction, and as such they are used to specify the position, velocity and momentum of a particle, or to specify a force. Vectors are usually denoted by boldface symbols (e.g. $\mathbf{u}$) or with an arrow above the symbol (e.g. $\vec{u}$). A tilde placed above or below the name of the vector is also commonly used in shorthand ($\tilde{u}$,$\underset{\sim}{u}$).

If we multiply a number a by a vector $\mathbf{v}$, we obtain a new vector that is parallel to the original but with a length that is a times the length of $\mathbf{v}$. If a is negative $a\mathbf{v}$ points in the opposite direction than $\mathbf{v}$. We can express any vector in terms of the so-called unit vectors. These vectors, which are designated $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$, have unit length and point along the positive x, y and z axis of the cartesian coordinate system (Figure 14.1.1). The symbol $\hat{\mathbf{i}}$ is read "i-hat". Hats are used to denote that a vector has unit length.

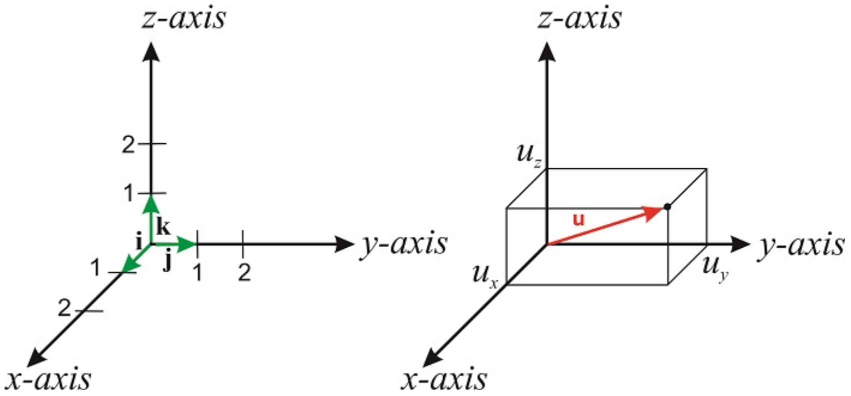


Figure 14.1.1: Left: The unit vectors. Right: A vector $\mathbf{u}$ can be expressed in terms of the unit vectors as $\mathbf{u}=u_x\hat{\mathbf{i}}+u_y\hat{j}+u_z\hat{\mathbf{k}}$ (CC BY-NC-SA; Marcia Levitus)

The length of $\mathbf{u}$ is its magnitude (or modulus), and is usually denoted by u:

$$u=|u|=(u_x^2+u_y^2+u_z^2)^{1/2} \tag{14.1.1}$$

If we have two vectors $\mathbf{u}=u_x\hat{\mathbf{i}}+u_y\hat{\mathbf{j}}+u_z\hat{\mathbf{k}}$ and $\mathbf{v}=v_x\hat{\mathbf{i}}+v_y\hat{\mathbf{j}}+v_z\hat{\mathbf{k}}$, we can add them to obtain

$$\mathbf{u}+\mathbf{v}=(u_x+v_x)\hat{\mathbf{i}}+(u_y+v_y)\hat{\mathbf{j}}+(u_z+v_z)\hat{\mathbf{k}}$$

or subtract them to obtain:

$$\mathbf{u}-\mathbf{v}=(u_x-v_x)\hat{\mathbf{i}}+(u_y-v_y)\hat{\mathbf{j}}+(u_z-v_z)\hat{\mathbf{k}}$$

When it comes to multiplication, we can perform the product of two vectors in two different ways. The first, which gives a scalar (a number) as the result, is called scalar product or dot product. The second, which gives a vector as a result, is called the vector (or cross) product. Both are important operations in physical chemistry.

14.2: The Scalar Product

The scalar product of vectors $\mathbf{u}$ and $\mathbf{v}$, also known as the dot product or inner product, is defined as (notice the dot between the symbols representing the vectors)

$$\mathbf{u}\cdot\mathbf{v}=|\mathbf{u}||\mathbf{v}|\cos\theta$$

where θ is the angle between the vectors. Notice that the dot product is zero if the two vectors are perpendicular to each other, and equals the product of their absolute values if they are parallel. It is easy to prove that

$$\mathbf{u}\cdot\mathbf{v}=u_xv_x+u_yv_y+u_zv_z$$

Example 14.2.1

Show that the vectors

$$\begin{aligned}\mathbf{u_1}&=\frac{1}{\sqrt{3}}\hat{\mathbf{i}}+\frac{1}{\sqrt{3}}\hat{\mathbf{j}}+\frac{1}{\sqrt{3}}\hat{\mathbf{k}}\\ \mathbf{u_2}&=\frac{1}{\sqrt{6}}\hat{\mathbf{i}}-\frac{2}{\sqrt{6}}\hat{\mathbf{j}}+\frac{1}{\sqrt{6}}\hat{\mathbf{k}}\\ \mathbf{u_3}&=-\frac{1}{\sqrt{2}}\hat{\mathbf{i}}+\frac{1}{\sqrt{2}}\hat{\mathbf{k}}\end{aligned}$$

are of unit length and are mutually perpendicular.

Solution

The length of the vectors are:

$$\begin{aligned}|\mathbf{u_1}|&=\left[\left(\frac{1}{\sqrt{3}}\right)^2+\left(\frac{1}{\sqrt{3}}\right)^2+\left(\frac{1}{\sqrt{3}}\right)^2\right]^{1/2}=\left[\frac{1}{3}+\frac{1}{3}+\frac{1}{3}\right]^{1/2}=1\\ |\mathbf{u_2}|&=\left[\left(\frac{1}{\sqrt{6}}\right)^2+\left(-\frac{2}{\sqrt{6}}\right)^2+\left(\frac{1}{\sqrt{6}}\right)^2\right]^{1/2}=\left[\frac{1}{6}+\frac{4}{6}+\frac{1}{6}\right]^{1/2}=1\\ |\mathbf{u_3}|&=\left[\left(-\frac{1}{\sqrt{2}}\right)^2+\left(\frac{1}{\sqrt{2}}\right)^2\right]^{1/2}=\left[\frac{1}{2}+\frac{1}{2}\right]^{1/2}=1\end{aligned}$$

To test if two vectors are perpendicular, we perform the dot product:

$$\begin{aligned}\mathbf{u_1}\cdot\mathbf{u_2}&=\left(\frac{1}{\sqrt{3}}\frac{1}{\sqrt{6}}-\frac{1}{\sqrt{3}}\frac{2}{\sqrt{6}}+\frac{1}{\sqrt{3}}\frac{1}{\sqrt{6}}\right)=0\\ \mathbf{u_1}\cdot\mathbf{u_3}&=\left(-\frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{3}}\frac{1}{\sqrt{2}}\right)=0\\ \mathbf{u_2}\cdot\mathbf{u_3}&=\left(-\frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}}+\frac{1}{\sqrt{6}}\frac{1}{\sqrt{2}}\right)=0\end{aligned}$$

Therefore, we just proved that the three pairs are mutually perpendicular, and the three vectors have unit length. In other words, these vectors are the vectors $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$ and $\hat{\mathbf{k}}$ rotated in space.

If the dot product of two vectors (of any dimension) is zero, we say that the two vectors are orthogonal. If the vectors have unit length, we say they are normalized. If two vectors are both normalized and they are orthogonal, we say they are orthonormal. The set of vectors shown in the previous example form an orthonormal set.[vectors:orthonormal] These concepts also apply to vectors that contain complex entries, but how do we perform the dot product in this case?

In general, the square of the modulus of a vector is

$$|\mathbf{u}|^2 = \mathbf{u}\cdot\mathbf{u} = u_x^2 + u_y^2 + u_z^2.$$

However, this does not work correctly for complex vectors. The square of i is -1, meaning that we risk having non-positive absolute values. To address this issue, we introduce a more general version of the dot product:

$$\mathbf{u}\cdot\mathbf{v} = u_x^* v_x + u_y^* v_y + u_z^* v_z,$$

where the "$*$" refers to the complex conjugate. Therefore, to calculate the modulus of a vector $\mathbf{u}$ that has complex entries, we use its complex conjugate:

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u}$$

✓ Example 14.2.2: Calculating the Modulus of a vector

Calculate the modulus of the following vector:

$$\mathbf{u} = \hat{\mathbf{i}} + i\hat{\mathbf{j}}$$

Solution

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u} = (\hat{\mathbf{i}} - i\hat{\mathbf{j}})(\hat{\mathbf{i}} + i\hat{\mathbf{j}}) = (1)(1) + (-i)(i) = 2 \rightarrow |\mathbf{u}| = \sqrt{2}$$

Analogously, if vectors contain complex entries, we can test whether they are orthogonal or not by checking the dot product $\mathbf{u}^* \cdot \mathbf{v}$.

✓ Example 14.2.3: Confirming orthogonality

Determine if the following pair of vectors are orthogonal (do not confuse the irrational number i with the unit vector $\hat{\mathbf{i}}$!)

$$\mathbf{u} = \hat{\mathbf{i}} + (1-i)\hat{\mathbf{j}}$$

and

$$\mathbf{v} = (1+i)\hat{\mathbf{i}} + \hat{\mathbf{j}}$$

Solution

$$\mathbf{u}^* \cdot \mathbf{v} = (\hat{\mathbf{i}} + (1+i)\hat{\mathbf{j}})((1+i)\hat{\mathbf{i}} + \hat{\mathbf{j}}) = (1)(1+i) + (1+i)(1) = 2 + 2i \neq 0$$

Therefore, the vectors are not orthogonal.

14.3: The Vector Product

The vector product of two vectors is a vector defined as

$$\mathbf{u} \times \mathbf{v} = |\mathbf{u}||\mathbf{v}|\mathbf{n}\sin\theta$$

where θ is again the angle between the two vectors, and $\mathbf{n}$ is the unit vector perpendicular to the plane formed by $\mathbf{u}$ and $\mathbf{v}$. The direction of the vector $\mathbf{n}$ is given by the right-hand rule. Extend your right hand and point your index finger in the direction of $\mathbf{u}$ (the vector on the left side of the $\times$ symbol) and your forefinger in the direction of $\mathbf{v}$. The direction of $\mathbf{n}$, which determines the direction of $\mathbf{u} \times \mathbf{v}$, is the direction of your thumb. If you want to revert the multiplication, and perform $\mathbf{v} \times \mathbf{u}$, you need to point your index finger in the direction of $\mathbf{v}$ and your forefinger in the direction of $\mathbf{u}$ (still using the right hand!). The resulting vector will point in the opposite direction (Figure $14.3.1$).

The magnitude of $\mathbf{u} \times \mathbf{v}$ is the product of the magnitudes of the individual vectors times $\sin\theta$. This magnitude has an interesting geometrical interpretation: it is the area of the parallelogram formed by the two vectors (Figure $14.3.1$).

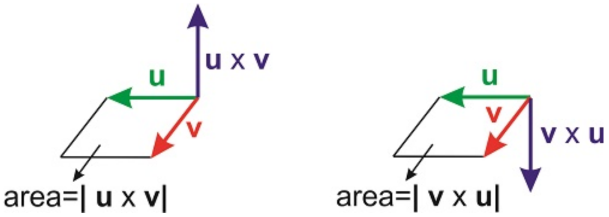


Figure 14.3.1: The vector product (CC BY-NC-SA; Marcia Levitus)

The cross product can also be expressed as a determinant:

$$\mathbf{u} \times \mathbf{v} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ u_x & u_y & u_z \\ v_x & v_y & v_z \end{vmatrix}$$

Example 14.3.1:

Given $\mathbf{u} = -2\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}}$ and $\mathbf{v} = 3\hat{\mathbf{i}} - \hat{\mathbf{j}} + \hat{\mathbf{k}}$, calculate $\mathbf{w} = \mathbf{u} \times \mathbf{v}$ and verify that the result is perpendicular to both $\mathbf{u}$ and $\mathbf{v}$.

Solution

$$\begin{aligned} \mathbf{u} \times \mathbf{v} &= \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ u_x & u_y & u_z \\ v_x & v_y & v_z \end{vmatrix} = \begin{vmatrix} \hat{\mathbf{i}} & \hat{\mathbf{j}} & \hat{\mathbf{k}} \\ -2 & 1 & 1 \\ 3 & -1 & 1 \end{vmatrix} \\ &= \hat{\mathbf{i}}(1+1) - \hat{\mathbf{j}}(-2-3) + \hat{\mathbf{k}}(2-3) \\ &= 2\hat{\mathbf{i}} + 5\hat{\mathbf{j}} - \hat{\mathbf{k}} \end{aligned}$$

To verify that two vectors are perpendicular we perform the dot product:

$$\mathbf{u} \cdot \mathbf{w} = (-2)(2) + (1)(5) + (1)(-1) = 0$$

$$\mathbf{v} \cdot \mathbf{w} = (3)(2) + (-1)(5) + (1)(-1) = 0$$

An important application of the cross product involves the definition of the angular momentum. If a particle with mass m moves a velocity $\mathbf{v}$ (a vector), its (linear) momentum is $\mathbf{p} = m\mathbf{v}$. Let $\mathbf{r}$ be the position of the particle (another vector), then the angular momentum of the particle is defined as

$$\mathbf{l} = \mathbf{r} \times \mathbf{p}$$

The angular momentum is therefore a vector perpendicular to both $\mathbf{r}$ and $\mathbf{p}$. Because the position of the particle needs to be defined with respect to a particular origin, this origin needs to be specified when defining the angular momentum.

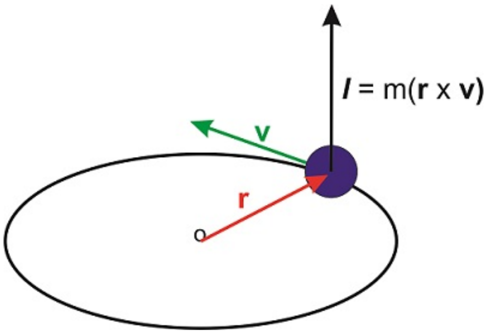


Figure 14.3.2: The angular momentum of a particle of position $\mathbf{r}$ from the origin and momentum $\mathbf{p} = m\mathbf{v}$ (CC BY-NC-SA; Marcia Levitus)

14.4: Vector Normalization

A vector of any given length can be divided by its modulus to create a unit vector (i.e. a vector of unit length). We will see applications of unit (or normalized) vectors in the next chapter.

For example, the vector

$$\mathbf{u}=\hat{\mathbf{i}}+\hat{\mathbf{j}}+i\hat{\mathbf{k}}$$

has a magnitude:

$$|\mathbf{u}|^2=1^2+1^2+(-i)(i)=3\rightarrow|\mathbf{u}|=\sqrt{3}$$

Therefore, to normalize this vector we divide all the components by its length:

$$\hat{\mathbf{u}}=\frac{1}{\sqrt{3}}\hat{\mathbf{i}}+\frac{1}{\sqrt{3}}\hat{\mathbf{j}}+\frac{i}{\sqrt{3}}\hat{\mathbf{k}}$$

Notice that we use the “hat” to indicate that the vector has unit length.

> Need help? The links below contain solved examples.
>
> Operations with vectors: http://tinyurl.com/mw4qmz8
>
> External links:
>
> - The dot product: http://patrickjmt.com/vectors-the-dot-product/
> - The cross product: http://patrickjmt.com/the-cross-product/
> - The dot and cross product: http://www.youtube.com/watch?v=enr7JqvehJs

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14.5: Problems

Problem 14.5.1

Given the following vectors in 3D:

$$\begin{aligned}\mathbf{v_1} &= \hat{\mathbf{i}} - 2\hat{\mathbf{j}} + \hat{\mathbf{k}} \\ \mathbf{v_2} &= \frac{1}{2}\hat{\mathbf{i}} - \frac{1}{2}\hat{\mathbf{k}} \\ \mathbf{v_3} &= i\hat{\mathbf{i}} + \hat{\mathbf{j}} + \hat{\mathbf{k}} \\ \mathbf{v_4} &= -\hat{\mathbf{i}} + i\hat{\mathbf{j}} + \hat{\mathbf{k}}\end{aligned}$$

Calculate:

1. $\mathbf{v_1} - 3\mathbf{v_2}$
2. $\mathbf{v_3} + \frac{1}{2}\mathbf{v_4}$
3. $\mathbf{v_1} \cdot \mathbf{v_2}$
4. $\mathbf{v_3} \cdot \mathbf{v_4}$
5. $\mathbf{v_1} \cdot \mathbf{v_3}$
6. $\mathbf{v_1} \times \mathbf{v_2}$
7. $|\mathbf{v_1}|$
8. $|\mathbf{v_2}|$
9. $|\mathbf{v_3}|$
10. $|\mathbf{v_4}|$
11. $\hat{\mathbf{v}}_\mathbf{2}$
12. $\hat{\mathbf{v}}_\mathbf{4}$

What is the angle between $\mathbf{v_1}$ and $\mathbf{v_2}$?

Are $\mathbf{v_3}$ and $\mathbf{v_4}$ orthogonal?

Write a vector orthogonal to both $\mathbf{v_1}$ and $\mathbf{v_2}$.

CHAPTER OVERVIEW

15: Matrices

Chapter Objectives

- Learn the nomenclature used in linear algebra to describe matrices (rows, columns, triangular matrices, diagonal matrices, trace, transpose, singularity, etc).
- Learn how to add, subtract and multiply matrices.
- Learn the concept of inverse.
- Understand the use of matrices as symmetry operators.
- Understand the concept of orthogonality.
- Understand how to calculate the eigenvalues and normalized eigenvectors of a 2×2 matrix.
- Understand the concept of Hermitian matrix

15.1: Definitions

An $m \times n$ matrix $\mathbf{A}$ is a rectangular array of numbers with m rows and n columns. The numbers m and n are the dimensions of $\mathbf{A}$. The numbers in the matrix are called its entries. The entry in row i and column j is called a_{ij}.

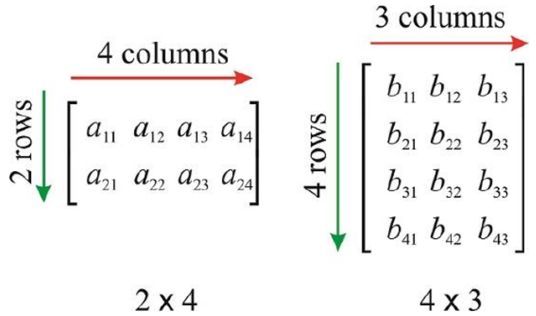

Figure 15.1.1: Matrices of different dimensions (CC BY-NC-SA; Marcia Levitus)

Some types of matrices have special names:

- A square matrix:

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix}$$

  with $m = n$
- A rectangular matrix:

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \end{pmatrix}$$

  with $m \neq n$
- A column vector:

$$\begin{pmatrix} 3 \\ 5 \\ -i \end{pmatrix}$$

  with $n = 1$
- A row vector:

$$\begin{pmatrix} 3 & -2 & 4 \end{pmatrix}$$

  with $m = 1$
- The identity matrix:

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

  with $a_{ij} = \delta_{i,j}$, where $\delta_{i,j}$ is a function defined as $\delta_{i,j} = 1$ if $i = j$ and $\delta_{i,j} = 0$ if $i \neq j$.
- A diagonal matrix:

$$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

  with $a_{ij} = c_i \delta_{i,j}$.
- An upper triangular matrix:

$$\begin{pmatrix} a & b & c \\ 0 & d & e \\ 0 & 0 & f \end{pmatrix}$$

All the entries below the main diagonal are zero.

- A lower triangular matrix:

$$\begin{pmatrix} a & 0 & 0 \\ b & c & 0 \\ d & e & f \end{pmatrix}$$

All the entries above the main diagonal are zero.

- A triangular matrix is one that is either lower triangular or upper triangular.

The Trace of a Matrix

The trace of an $n \times n$ square matrix $\mathbf{A}$ is the sum of the diagonal elements, and formally defined as $Tr(\mathbf{A}) = \sum_{i=1}^{n} a_{ii}$.

For example,

$$\mathbf{A} = \begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix} ; Tr(\mathbf{A}) = 12 + 3i$$

Singular and Nonsingular Matrices

A square matrix with nonzero determinant is called *nonsingular*. A matrix whose determinant is zero is called *singular*. (Note that you cannot calculate the determinant of a non-square matrix).

The Matrix Transpose

The matrix transpose, most commonly written $\mathbf{A}^T$, is the matrix obtained by exchanging $\mathbf{A}$'s rows and columns. It is obtained by replacing all elements a_{ij} with a_{ji}. For example:

$$\mathbf{A} = \begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \end{pmatrix} \rightarrow \mathbf{A}^T = \begin{pmatrix} 3 & 5 \\ -2 & 3i \\ 4 & 3 \end{pmatrix}$$

15.2: Matrix Addition

The sum of two matrices $\mathbf{A}$ and $\mathbf{B}$ (of the same dimensions) is a new matrix of the same dimensions, $\mathbf{C} = \mathbf{A} + \mathbf{B}$. The sum is defined by adding entries with the same indices: $c_{ij} = a_{ij} + b_{ij}$.

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix} + \begin{pmatrix} 0 & 2 & 1 \\ -4 & -2i & i \\ -i & 1/2 & -5 \end{pmatrix} = \begin{pmatrix} 3 & 0 & 5 \\ 1 & i & 3+i \\ -2i & 1 & 4 \end{pmatrix}$$

Need help? The link below contains solved examples: Matrix addition: http://tinyurl.com/m5skvpy

External links:

- Matrices: Basic Matrix Operations (add, subtract, multiply by constant) http://patrickjmt.com/matrices-basic-matrix-operations-add-subtract-multiply-by-constant/

15.3: Matrix Multiplication

If $\mathbf{A}$ has dimensions $m \times n$ and $\mathbf{B}$ has dimensions $n \times p$, then the product $\mathbf{AB}$ is defined, and has dimensions $m \times p$.

The entry $(ab)_{ij}$ is obtained by multiplying row i of $\mathbf{A}$ by column j of $\mathbf{B}$, which is done by multiplying corresponding entries together and then adding the results:

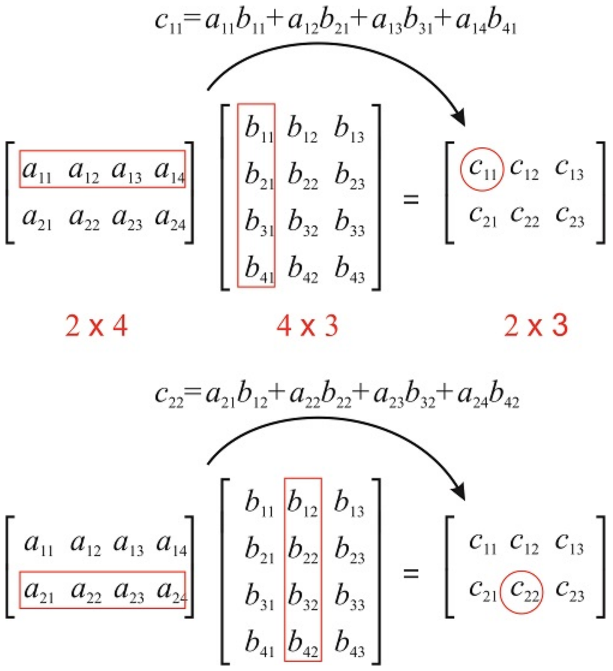

Figure 15.3.1: Matrix multiplication (CC BY-NC-SA; Marcia Levitus)

Example 15.3.1

Calculate the product

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix}$$

Solution

We need to multiply a 3×3 matrix by a 3×2 matrix, so we expect a 3×2 matrix as a result.

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix}$$

To calculate a, which is entry (1,1), we use row 1 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow a = 1 \times 1 + (-2) \times 5 + 4 \times (-1) = -13$$

To calculate b, which is entry (1,2), we use row 1 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow b = 1 \times 0 + (-2) \times 3 + 4 \times 0 = -6$$

To calculate c, which is entry (2,1), we use row 2 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow c = 5 \times 1 + 0 \times 5 + 3 \times (-1) = 2$$

To calculate d, which is entry (2,2), we use row 2 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow d = 5 \times 0 + 0 \times 3 + 3 \times 0 = 0$$

To calculate e, which is entry (3,1), we use row 3 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow e = 0 \times 1 + 1/2 \times 5 + 9 \times (-1) = -13/2$$

To calculate f, which is entry (3,2), we use row 3 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow f = 0 \times 0 + 1/2 \times 3 + 9 \times 0 = 3/2$$

The result is:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} -13 & -6 \\ 2 & 0 \\ -13/2 & 3/2 \end{pmatrix}$$

✓ Example 15.3.2

Calculate

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix}$$

Solution

We are asked to multiply a 2×3 matrix by a 3×1 matrix (a column vector). The result will be a 2×1 matrix (a vector).

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$a = 1 \times 1 + (-2) \times 5 + 4 \times (-1) = -13$$

$$b = 5 \times 1 + 0 \times 5 + 3 \times (-1) = 2$$

The solution is:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} -13 \\ 2 \end{pmatrix}$$

Need help? The link below contains solved examples: Multiplying matrices of different shapes (three examples): http://tinyurl.com/kn8ysqq

External links:

- Multiplying matrices, example 1: http://patrickjmt.com/matrices-multiplying-a-matrix-by-another-matrix/

- Multiplying matrices, example 2: http://patrickjmt.com/multiplying-matrices-example-2/
- Multiplying matrices, example 3: http://patrickjmt.com/multiplying-matrices-example-3/

The Commutator

Matrix multiplication is not, in general, commutative. For example, we can perform

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} -13 \\ 2 \end{pmatrix}$$

but cannot perform

$$\begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} \begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix}$$

Even with square matrices, that can be multiplied both ways, multiplication is not commutative. In this case, it is useful to define the **commutator**, defined as:

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$$

Example 15.3.3

Given $\mathbf{A} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix}$ and $\mathbf{B} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix}$

Calculate the commutator $[\mathbf{A}, \mathbf{B}]$

Solution

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$$

$$\mathbf{AB} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} = \begin{pmatrix} 3 \times 1 + 1 \times (-1) & 3 \times 0 + 1 \times 2 \\ 2 \times 1 + 0 \times (-1) & 2 \times 0 + 0 \times 2 \end{pmatrix} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix}$$

$$\mathbf{BA} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} = \begin{pmatrix} 1 \times 3 + 0 \times 2 & 1 \times 1 + 0 \times 0 \\ -1 \times 3 + 2 \times 2 & -1 \times 1 + 2 \times 0 \end{pmatrix} = \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix} - \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

Multiplication of a vector by a scalar

The multiplication of a vector $\vec{v_1}$ by a scalar n produces another vector of the same dimensions that lies in the same direction as $\vec{v_1}$;

$$n \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} nx \\ ny \end{pmatrix}$$

The scalar can stretch or compress the length of the vector, but cannot rotate it (figure [fig:vector_by_scalar]).

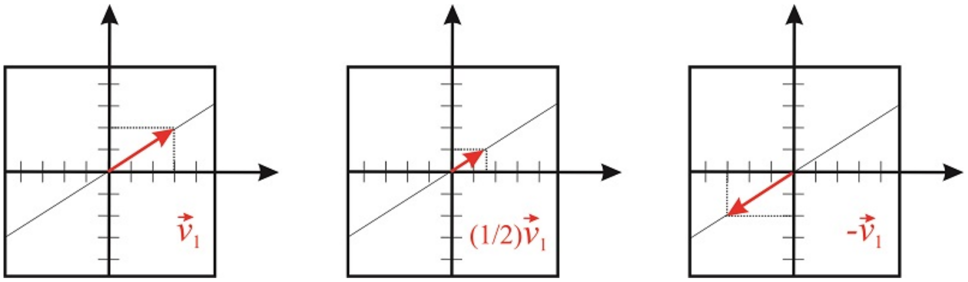

Figure 15.3.2: Multiplication of a vector by a scalar (CC BY-NC-SA; Marcia Levitus)

Multiplication of a square matrix by a vector

The multiplication of a vector $\vec{v_1}$ by a square matrix produces another vector of the same dimensions of $\vec{v_1}$. For example, we can multiply a 2×2 matrix and a 2-dimensional vector:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} ax + by \\ cx + dy \end{pmatrix}$$

For example, consider the matrix

$$\mathbf{A} = \begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}$$

The product

$$\begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

is

$$\begin{pmatrix} -2x \\ y \end{pmatrix}$$

We see that 2×2 matrices act as operators that transform one 2-dimensional vector into another 2-dimensional vector. This particular matrix keeps the value of y constant and multiplies the value of x by -2 (Figure $15.3.3$).

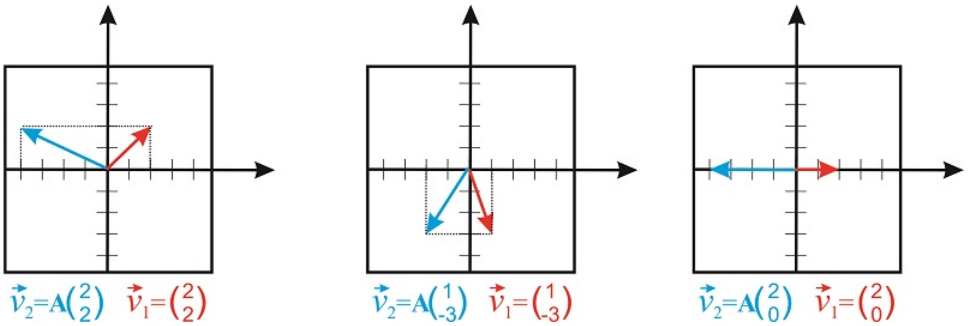

Figure 15.3.3: Multiplication of a vector by a square matrix (CC BY-NC-SA; Marcia Levitus)

Notice that matrices are useful ways of representing operators that change the orientation and size of a vector. An important class of operators that are of particular interest to chemists are the so-called symmetry operators.

15.4: Symmetry Operators

The symmetry of molecules is essential for understanding the structures and properties of organic and inorganic compounds. The properties of chemical compounds are often easily explained by consideration of symmetry. For example, the symmetry of a molecule determines whether the molecule has a permanent dipole moment or not. The theories that describe optical activity, infrared and ultraviolet spectroscopy, and crystal structure involve the application of symmetry considerations. Matrix algebra is the most important mathematical tool in the description of symmetry.

A symmetry operation, such as a rotation around a symmetry axis or a reflection through a plane, is an operation that, when performed on an object, results in a new orientation of the object that is indistinguishable from the original. For example, if we rotate a square in the plane by $\pi/2$ or π the new orientation of the square is superimposable on the original one (Figure $15.4.1$).

If rotation by an angle θ of a molecule (or object) about some axis results in an orientation of the molecule (or object) that is superimposable on the original, the axis is called a rotation axis. The molecule (or object) is said to have an n-fold rotational axis, where n is $2\pi/\theta$. The axis is denoted as C_n. The square of Figure $15.4.1$ has a C_4 axis perpendicular to the plane because a 90° rotation leaves the figure indistinguishable from the initial orientation. This axis is also a C_2 axis because a 180° degree rotation leaves the square indistinguishable from the original square. In addition, the figure has several other C_2 axis that lie on the same plane as the square:

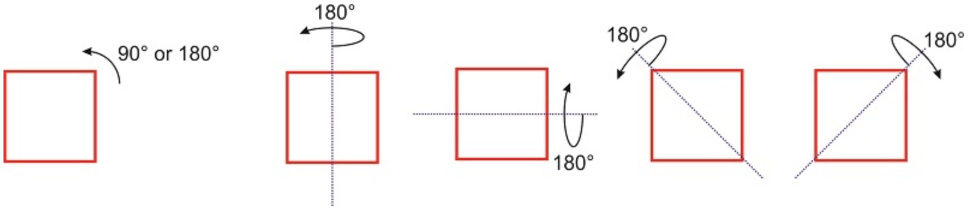

Figure 15.4.1: Symmetry operations performed on a square (CC BY-NC-SA; Marcia Levitus)

A symmetry operation moves all the points of the object from one initial position to a final position, and that means that symmetry operators are 3×3 square matrices (or 2×2 in two dimensions). The following equation represents the action of a symmetry operator $\hat{A}$ on the location of the point (x,y,z) (a vector):

$$\hat{A}(x,y,z)=(x',y',z')$$

The vector (x',y',z') represents the location of the point after the symmetry operation. Let's come back to the rotation axes we discussed before. A 2-fold rotation around the $z-$axis changes the location of a point (x,y,z) to $(-x,-y,z)$ (see Figure $15.4.2$). By convention, rotations are always taken in the counterclockwise direction.

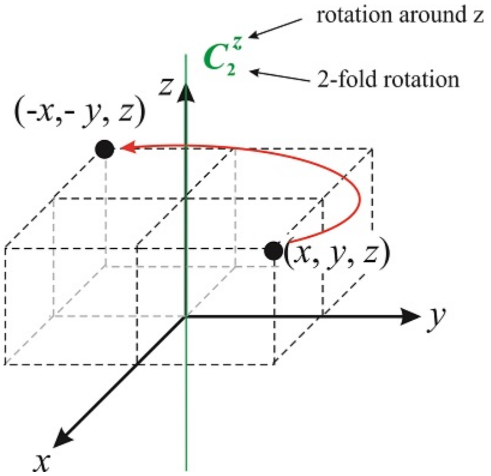

Figure 15.4.2: A 2-fold rotation around the z-axis (CC BY-NC-SA; Marcia Levitus)

What is the matrix that represents the operator $\hat{C}_2^z$? The matrix transforms the vector (x,y,z) into $(-x,-y,z)$, so

$$\hat{C}_2^z(x,y,z)=(-x,-y,z)$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

We know the matrix is a 3×3 square matrix because it needs to multiply a 3-dimensional vector. In addition, we write the vector as a vertical column to satisfy the requirements of matrix multiplication.

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$a_{11}x + a_{12}y + a_{13}z = -x$$

$$a_{21}x + a_{22}y + a_{23}z = -y$$

$$a_{31}x + a_{32}y + a_{33}z = z$$

and we conclude that $a_{11} = -1$, $a_{12} = a_{13} = 0$, $a_{22} = -1$, $a_{21} = a_{23} = 0$ and $a_{33} = 1$, $a_{31} = a_{32} = 0$:

$$\hat{C_2^z} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Rotations are not the only symmetry operations we can perform on a molecule. Figure $15.4.3$ illustrates the reflection of a point through the xz plane. This operation transforms the vector (x, y, z) into the vector $(x, -y, z)$. Symmetry operators involving reflections through a plane are usually denoted with the letter σ, so the operator that reflects a point through the xz plane is $\hat{\sigma}_{xz}$:

$$\hat{\sigma}_{xz}(x, y, z) = (x, -y, z)$$

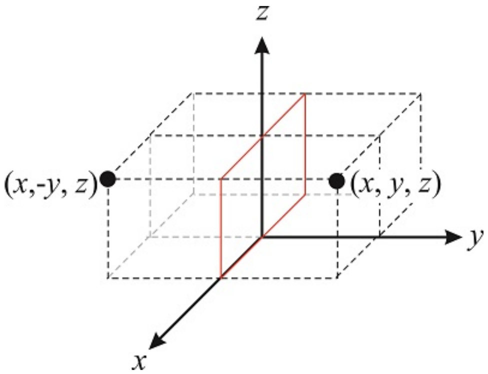

Figure 15.4.3: A reflection through the xz plane (CC BY-NC-SA; Marcia Levitus)

Following the same logic we used for the rotation matrix, we can write the $\hat{\sigma}_{xz}$ operator as:

$$\hat{\sigma}_{x,z} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This is true because

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

As we said before, the symmetry properties of molecules are essential for understanding the structures and properties of organic and inorganic compounds. For example, those of you who took organic chemistry know that molecules that have an inversion center (Problem 15.3) do not have permanent dipole moments. The symmetry of molecules is also related to their abilities to absorb light. Figure $15.4.4$ shows the three symmetry elements of the molecule of water (H_2O). This molecule has only one rotation axis, which is 2-fold, and therefore we call it a "C_2 axis". It also has two mirror planes, one that contains the two hydrogen atoms (σ_{yz}), and another one perpendicular to it (σ_{xz}). Both planes contain the C_2 axis.

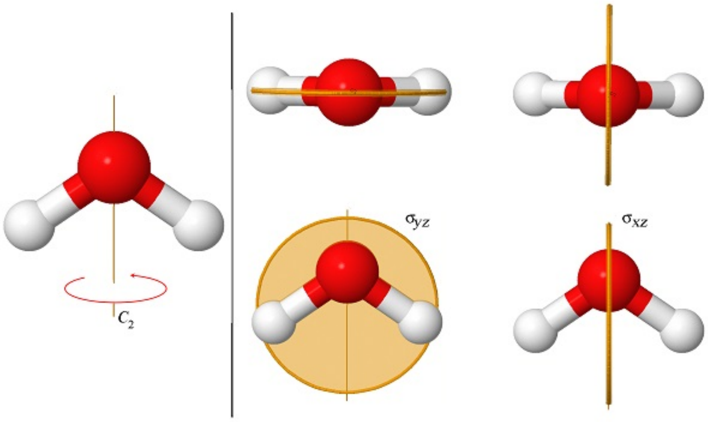

Figure 15.4.4: The symmetry elements of the molecule of water (CC BY-NC-SA; Marcia Levitus)

As you will learn in your inorganic chemistry course, chemists organize molecules that share the same symmetry elements under a common group. For example, the group that contains molecules with these three symmetry elements is called "the C_{2v} group". Because the inversion operation (Problem 15.3) is not part of this group we know that all C_{2v} molecules are polar.

The molecule of methane (CH_4) has several symmetry elements, some of which we have not learned in this chapter. One that is relatively easy to identify is the C_3 rotation axis (Figure 15.4.5):

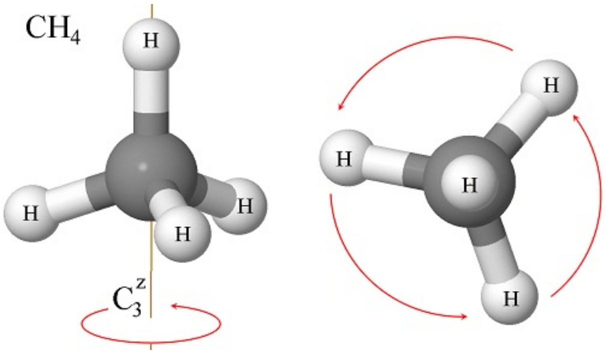

Figure 15.4.5: The C_3 axis of the molecule of methane (CC BY-NC-SA; Marcia Levitus)

Can we write the matrix for the operator that corresponds to the 3-fold rotation? If we look at the molecule from the top, so the z-axis is perpendicular to the plane of the paper (or screen if you are reading this in a computer), we see that the rotation moves one hydrogen atom from one vertex of an equilateral triangle to the other one in a counterclockwise fashion. Therefore, we need a matrix that will move these vertices as shown in the figure:

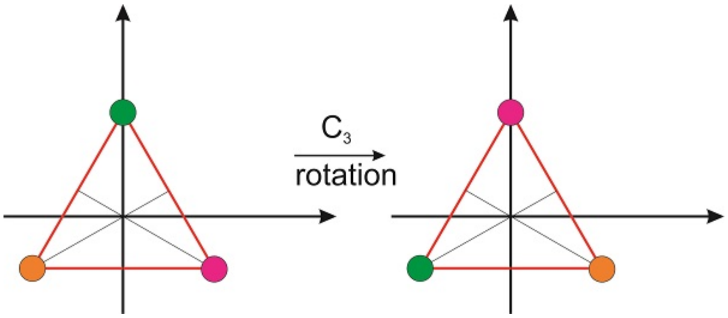

Figure 15.4.6: A 3-fold rotation around the axis perpendicular to the plane that contains the triangle. (CC BY-NC-SA; Marcia Levitus)

We need the coordinates of the three vertices, which can be obtained from simple geometrical arguments. If we place the green vertex at $x = 0$ and $y = h$, then the position of the magenta vertex is $x = h \times \cos 30^\circ$ and $y = -h \times \sin 30^\circ$ and the position of the orange vertex is $-x = h \times \cos 30^\circ$ and $y = -h \times \sin 30^\circ$ (Figure 15.4.7).

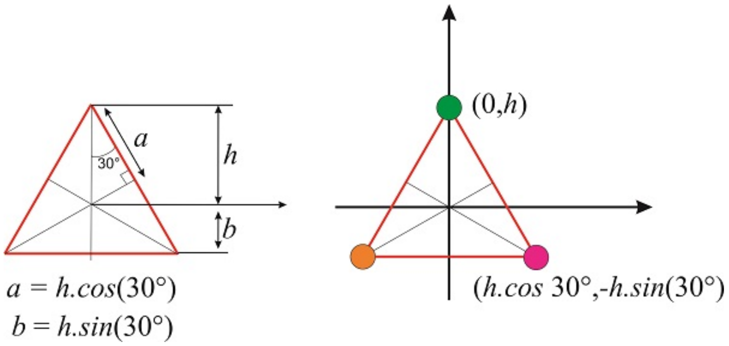

Figure 15.4.7: A 3-fold rotation around the axis perpendicular to the plane that contains the triangle. (CC BY-NC-SA; Marcia Levitus)

The matrix we are looking for needs to rotate the magenta circle until it overlaps with the green circle:

$$\hat{C}_3(h\sqrt{3}/2, -h/2, z) = (0, h, z)$$

where we note that this rotation does not change the value of z.

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} h\sqrt{3}/2 \\ -h/2 \\ z \end{pmatrix} = \begin{pmatrix} 0 \\ h \\ z \end{pmatrix}$$

Here, we have used the fact that $\cos 30^\circ = \sqrt{3}/2$ and $\sin 30^\circ = 1/2$.

Multiplying the matrix by the vector:

$$a_{11}h\sqrt{3}/2 - a_{12}h/2 + a_{13}z = 0$$

$$a_{21}h\sqrt{3}/2 - a_{22}h/2 + a_{23}z = h$$

$$a_{31}h\sqrt{3}/2 - a_{32}h/2 + a_{33}z = z$$

From these equations, we conclude that $a_{13} = a_{23} = a_{31} = a_{32} = 0$, $a_{12} = \sqrt{3}a_{11}$, and $a_{22} = \sqrt{3}a_{21} - 2$. So far the matrix looks like:

$$\hat{C}_3 = \begin{pmatrix} a_{11} & \sqrt{3}a_{11} & 0 \\ a_{21} & \sqrt{3}a_{21} - 2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

To find the remaining entries let's apply the matrix to the vector $(0, h, z)$, which needs to rotate to $(-h\sqrt{3}/2, -h/2, z)$:

$$\begin{pmatrix} a_{11} & \sqrt{3}a_{11} & 0 \\ a_{21} & \sqrt{3}a_{21} - 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ h \\ z \end{pmatrix} = \begin{pmatrix} -h\sqrt{3}/2 \\ -h/2 \\ z \end{pmatrix}$$

From this multiplication we get

$$\sqrt{3}a_{11}h = -h\sqrt{3}/2 \rightarrow a_{11} = -1/2$$

$$(\sqrt{3}a_{21} - 2)h = -h/2 \rightarrow a_{21} = \sqrt{3}/2$$

and therefore,

$$\hat{C}_3 = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

15.5: Matrix Inversion

The inverse of a square matrix $\mathbf{A}$, sometimes called a reciprocal matrix, is a matrix $\mathbf{A}^{-1}$ such that $\mathbf{A}\mathbf{A}^{-1}=\mathbf{I}$, where $\mathbf{I}$ is the identity matrix.

It is easy to obtain $\mathbf{A}^{-1}$ in the case of a 2×2 matrix:

$$\mathbf{A}=\begin{pmatrix} a & b \\ c & d \end{pmatrix};\ \mathbf{A}^{-1}=\begin{pmatrix} e & f \\ g & h \end{pmatrix}$$

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} e & f \\ g & h \end{pmatrix}=\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$ae+bg=1 \tag{15.5.1}$$

$$af+bh=0 \tag{15.5.2}$$

$$ce+dg=0 \tag{15.5.3}$$

$$cf+dh=1 \tag{15.5.4}$$

From Equations 15.5.1 and 15.5.3: $g=(1-ae)/b=-ce/d\rightarrow ae=cbe/d+1\rightarrow e\,(a-cb/d)=1\rightarrow e\,(ad-cb)=d\rightarrow e=d/(ad-cb)$. You can obtain expressions for f, g and h in a similar way to obtain:

$$\mathbf{A}^{-1}=\frac{1}{ad-bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$$

Notice that the term $(ad-bc)$ is the determinant of $\mathbf{A}$, and therefore $\mathbf{A}^{-1}$ exists only if $|\mathbf{A}|\neq 0$. In other words, the inverse of a singular matrix is not defined.

If you think about a square matrix as an operator, the inverse “undoes” what the original matrix does. For example, the matrix $\begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}$, when applied to a vector (x,y), gives $(-2x,y)$:

$$\begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix}=\begin{pmatrix} -2x \\ y \end{pmatrix}$$

The inverse of $\mathbf{A}$, when applied to $(-2x,y)$, gives back the original vector, (x,y):

$$\mathbf{A}^{-1}=\frac{1}{ad-bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}\rightarrow \mathbf{A}^{-1}=-\frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -2 \end{pmatrix}$$

$$-\frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -2 \end{pmatrix}\begin{pmatrix} -2x \\ y \end{pmatrix}=\begin{pmatrix} x \\ y \end{pmatrix}$$

It is of course possible to calculate the inverse of matrices of higher dimensions, but in this course you will not be required to do so by hand.

15.6: Orthogonal Matrices

A nonsingular matrix is called orthogonal when its inverse is equal to its transpose:

$$\mathbf{A}^T=\mathbf{A}^{-1}\rightarrow\mathbf{A}^T\mathbf{A}=\mathbf{I}.$$

For example, for the matrix

$$\mathbf{A}=\begin{pmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{pmatrix},$$

the inverse is

$$\mathbf{A}^{-1}=\begin{pmatrix}\cos\theta & \sin\theta\\ -\sin\theta & \cos\theta\end{pmatrix}=\mathbf{A}^T$$

We do not need to calculate the inverse to see if the matrix is orthogonal. We can transpose the matrix, multiply the result by the matrix, and see if we get the identity matrix as a result:

$$\mathbf{A}^T=\begin{pmatrix}\cos\theta & \sin\theta\\ -\sin\theta & \cos\theta\end{pmatrix}$$

$$\mathbf{A}^T\mathbf{A}=\begin{pmatrix}\cos\theta & \sin\theta\\ -\sin\theta & \cos\theta\end{pmatrix}\begin{pmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{pmatrix}=\begin{pmatrix}(\cos^2\theta+\sin^2\theta) & 0\\ 0 & (\sin^2\theta+\cos^2\theta)\end{pmatrix}=\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}$$

The columns of orthogonal matrices form a system of orthonormal vectors (Section 14.2):

$$\mathbf{M}=\begin{pmatrix}a_1 & b_1 & c_1\\ a_2 & b_2 & c_2\\ a_3 & b_3 & c_3\end{pmatrix}\rightarrow\mathbf{a}=\begin{pmatrix}a_1\\ a_2\\ a_3\end{pmatrix};\ \mathbf{b}=\begin{pmatrix}b_1\\ b_2\\ b_3\end{pmatrix};\ \mathbf{c}=\begin{pmatrix}c_1\\ c_2\\ c_3\end{pmatrix}$$

$$\mathbf{a}\cdot\mathbf{b}=\mathbf{a}\cdot\mathbf{c}=\mathbf{c}\cdot\mathbf{b}=0$$

$$|\mathbf{a}|=|\mathbf{b}|=|\mathbf{c}|=1$$

✓ Example 15.6.1

Prove that the matrix $\mathbf{M}$ is an orthogonal matrix and show that its columns form a set of orthonormal vectors.

$$\mathbf{M}=\begin{pmatrix}2/3 & 1/3 & -2/3\\ 2/3 & -2/3 & 1/3\\ 1/3 & 2/3 & 2/3\end{pmatrix}$$

Note: This problem is also available in video format: http://tinyurl.com/k2tkny5

Solution

We first need to prove that $\mathbf{M}^T\mathbf{M}=1$

$$\mathbf{M}=\begin{pmatrix}\color{red}{2/3} & \color{blue}{1/3} & -2/3\\ \color{red}{2/3} & \color{blue}{-2/3} & 1/3\\ \color{red}{1/3} & \color{blue}{2/3} & 2/3\end{pmatrix}\rightarrow\mathbf{M}^T=\begin{pmatrix}\color{red}{2/3} & \color{red}{2/3} & \color{red}{1/3}\\ \color{blue}{1/3} & \color{blue}{-2/3} & \color{blue}{2/3}\\ -2/3 & 1/3 & 2/3\end{pmatrix}$$

$$\mathbf{M}^T\mathbf{M}=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}=\mathbf{I}$$

Because $\mathbf{M}^T\mathbf{M}=\mathbf{I}$, the matrix is orthogonal.

We now how to prove that the columns for a set of orthonormal vectors. The vectors are:

$$\mathbf{a}=2/3\mathbf{i}+2/3\mathbf{j}+1/3\mathbf{i}=\begin{pmatrix}2/3\\2/3\\1/3\end{pmatrix}$$

$$\mathbf{b}=1/3\mathbf{i}-2/3\mathbf{j}+2/3\mathbf{i}=\begin{pmatrix}1/3\\-2/3\\2/3\end{pmatrix}$$

$$\mathbf{c}=-2/3\mathbf{i}+1/3\mathbf{j}+2/3\mathbf{i}=\begin{pmatrix}-2/3\\1/3\\2/3\end{pmatrix}$$

The modulii of these vectors are:

$$|\mathbf{a}|^2=(2/3)^2+(2/3)^2+(1/3)^2=1$$

$$|\mathbf{b}|^2=(1/3)^2+(-2/3)^2+(2/3)^2=1$$

$$|\mathbf{c}|^2=(-2/3)^2+(1/3)^2+(2/3)^2=1$$

which proves that the vectors are normalized.

The dot products of the three pairs of vectors are:

$$\mathbf{a}\cdot\mathbf{b}=(2/3)(1/3)+(2/3)(-2/3)+(1/3)(2/3)=0$$

$$\mathbf{a}\cdot\mathbf{c}=(2/3)(-2/3)+(2/3)(1/3)+(1/3)(2/3)=0$$

$$\mathbf{c}\cdot\mathbf{b}=(-2/3)(1/3)+(1/3)(-2/3)+(2/3)(2/3)=0$$

which proves they are mutually orthogonal.

Because the vectors are normalized and mutually orthogonal, they form an orthonormal set.

Orthogonal matrices, when thought as operators that act on vectors, are important because they produce transformations that preserve the lengths of the vectors and the relative angles between them. For example, in two dimensions, the matrix

$$\mathbf{M}_1=1/\sqrt{2}\begin{pmatrix}1&1\\1&-1\end{pmatrix}$$

is an operator that rotates a vector by $\pi/4$ in the counterclockwise direction (Figure $15.6.1$) preserving the lengths of the vectors and their relative orientation. In other words, an orthogonal matrix rotates a shape without distorting it. If the columns are orthogonal vectors that are not normalized, as in

$$\mathbf{M}_2=\begin{pmatrix}1&1\\1&-1\end{pmatrix},$$

the object changes in size but the shape is not distorted. If, however, the two columns are non-orthogonal vectors, the transformation will distort the shape. Figure $15.6.1$ shows an example with the matrix

$$\mathbf{M}_3=\begin{pmatrix}1&2\\-1&1\end{pmatrix}$$

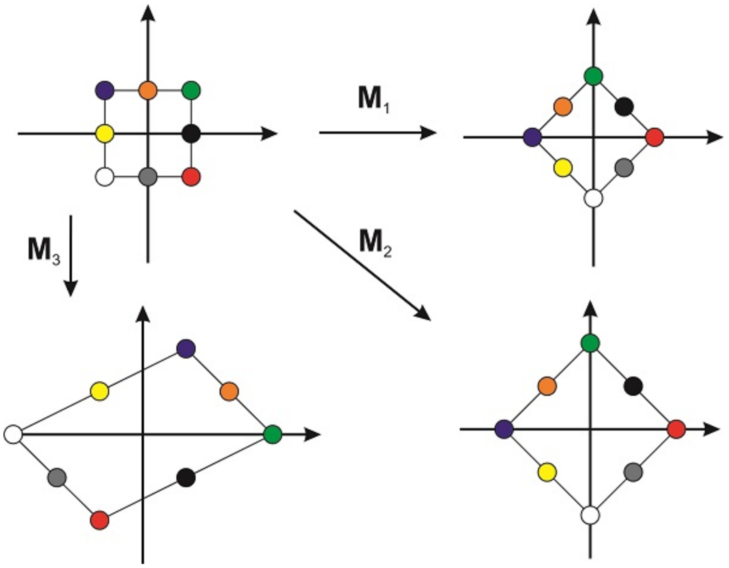

Figure 15.6.1: Orthogonal (M_1) and non-orthogonal ($M_{2,3}$) transformations. An orthogonal transformation preserves the lengths of the vectors and their relative orientations. (CC BY-NC-SA; Marcia Levitus)

From this discussion, it should not surprise you that all the matrices that represent symmetry operators (Section 15.4) are orthogonal matrices. These operators are used to rotate and reflect the object around different axes and planes without distorting its size and shape.

15.7: Eigenvalues and Eigenvectors

Since square matrices are operators, it should not surprise you that we can determine its eigenvalues and eigenvectors. The eigenvectors are analogous to the eigenfunctions we discussed in Chapter 11.

If $\mathbf{A}$ is an $n \times n$ matrix, then a nonzero vector $\mathbf{x}$ is called an eigenvector of $\mathbf{A}$ if $\mathbf{Ax}$ is a scalar multiple of $\mathbf{x}$:

$$\mathbf{Ax} = \lambda\mathbf{x}$$

The scalar λ is called the eigenvalue of $\mathbf{A}$, and $\mathbf{x}$ is said to be an eigenvector. For example, the vector $(2,0)$ is an eigenvector of

$$\mathbf{A} = \begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}$$

with eigenvalue $\lambda = -2$:

$$\begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 2 \\ 0 \end{pmatrix} = -2\begin{pmatrix} 2 \\ 0 \end{pmatrix}$$

Notice that the matrix $\mathbf{A}$, like any other 2×2 matrix, transforms a 2-dimensional vector into another one that in general will lie on a different direction. For example, if we take $(2,2)$, this matrix will transform it into $\mathbf{A}(2,2) = (-4,2)$, which has a different orientation. However, the vector $(2,0)$ is special, because this matrix transforms it in a vector that is a multiple of itself: $\mathbf{A}(2,0) = (-4,0)$. For this particular vector, the matrix behaves as a number! (in this case the number -2). In fact, we have a whole family of vectors that do the same: $\mathbf{A}(x,0) = (-4x,0)$, or in other words, any vector parallel to the $x-$axis. There is another family of vectors that makes $\mathbf{A}$ behave as a number: $\mathbf{A}(0,y) = (0,y)$, or in other words, any vector parallel to the $y-$axis makes $\mathbf{A}$ behave as the number 1.

The argument above gives a geometrical interpretation to eigenvectors and eigenvalues. For a 2×2 matrix, there are two ‘special’ lines in the plane. If we take a vector along one of these lines, the matrix behaves as a number we call the eigenvalue, and simply shrinks or expands the vector without changing its direction.

✓ Example 15.7.1

The vectors $\mathbf{x}_1 = (-i,1)$ and $\mathbf{x}_2 = (i,1)$ are the two eigenvectors of

$$\mathbf{A} = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$

What are the corresponding eigenvalues?

Solution

By definition:

$$\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} -i \\ 1 \end{pmatrix} = \lambda_1\begin{pmatrix} -i \\ 1 \end{pmatrix}$$

where λ_1 is the eigenvector corresponding to $\mathbf{x}_1$

We have:

$$\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} -i \\ 1 \end{pmatrix} = \begin{pmatrix} -i+1 \\ i+1 \end{pmatrix} = (1+i)\begin{pmatrix} -i \\ 1 \end{pmatrix}$$

and therefore $\lambda_1 = (1+i)$.

For the second eigenvector:

$$\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} i \\ 1 \end{pmatrix} = \lambda_2\begin{pmatrix} i \\ 1 \end{pmatrix}$$

where λ_2 is the eigenvector corresponding to $\mathbf{x}_2$

We have:

$$\begin{pmatrix}1 & 1\\ -1 & 1\end{pmatrix}\begin{pmatrix}i\\ 1\end{pmatrix}=\begin{pmatrix}i+1\\ -i+1\end{pmatrix}=(1-i)\begin{pmatrix}i\\ 1\end{pmatrix}$$

and therefore $\lambda_2=(1-i)$.

The obvious question now is how to find the eigenvalues of a matrix. We will concentrate on 2×2 matrices, although there are of course methods to do the same in higher dimensions.

Let’s say that we want to find the eigenvectors of

$$\mathbf{A}=\begin{pmatrix}3 & 2\\ -1 & 0\end{pmatrix}$$

The eigenvectors satisfy the following equation:

$$\begin{pmatrix}3 & 2\\ -1 & 0\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=\lambda\begin{pmatrix}x\\ y\end{pmatrix}$$

Our first step will be to multiply the right side by the identity matrix. This is analogous to multiplying by the number 1, so it does nothing:

$$\begin{pmatrix}3 & 2\\ -1 & 0\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=\lambda\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}$$

We will now group all terms on the left side:

$$\begin{pmatrix}3 & 2\\ -1 & 0\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}-\lambda\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=0$$

distribute λ:

$$\begin{pmatrix}3 & 2\\ -1 & 0\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}-\begin{pmatrix}\lambda & 0\\ 0 & \lambda\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=0$$

and group the two matrices in one:

$$\begin{pmatrix}3-\lambda & 2\\ -1 & 0-\lambda\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=0$$

multiplying the matrix by the vector:

$$(3-\lambda)x+2y=0$$

$$-x-\lambda y=0$$

which gives:

$$\begin{aligned}(3-\lambda)(-\lambda y)+2y &=0\\ y[(3-\lambda)(-\lambda)+2] &=0\end{aligned}$$

We do not want to force y to be zero, because we are trying to determine the eigenvector, which may have $y\neq 0$. Then, we conclude that

$$[(3-\lambda)(-\lambda)+2]=0 \tag{15.7.1}$$

which is a quadratic equation in λ. Now, note that $[(3-\lambda)(-\lambda)+2]$ is the determinant

$$\begin{vmatrix}3-\lambda & 2\\ -1 & -\lambda\end{vmatrix}$$

We just concluded that in order to solve

$$\begin{pmatrix}3-\lambda & 2\\ -1 & 0-\lambda\end{pmatrix}\begin{pmatrix}x\\ y\end{pmatrix}=0$$

we just need to look at the values of λ that make the determinant of the matrix equal to zero:

$$\begin{vmatrix} 3-\lambda & 2 \\ -1 & -\lambda \end{vmatrix} = 0$$

Equation 15.7.1 is called the *characteristic equation* of the matrix, and in the future we can skip a few steps and write it down directly.

Let's start the problem from scratch. Let's say that we want to find the eigenvectors of

$$\mathbf{A} = \begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix}$$

We just need to subtract λ from the main diagonal, and set the determinant of the resulting matrix to zero:

$$\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 3-\lambda & 2 \\ -1 & 0-\lambda \end{pmatrix} \rightarrow \begin{vmatrix} 3-\lambda & 2 \\ -1 & -\lambda \end{vmatrix} = 0$$

We get a quadratic equation in λ:

$$\begin{vmatrix} 3-\lambda & 2 \\ -1 & -\lambda \end{vmatrix} = (3-\lambda)(-\lambda) + 2 = 0$$

which can be solved to obtain the two eigenvalues: $\lambda_1 = 1$ and $\lambda_2 = 2$.

Our next step is to obtain the corresponding eigenvectors, which satisfy:

$$\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = 1 \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$$

for λ_1

$$\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = 2 \begin{pmatrix} x_2 \\ y_2 \end{pmatrix}$$

for λ_2

Let's solve both side by side:

$\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = 1 \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$ $\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = 1 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$ $\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} - 1 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = 0$ $\begin{pmatrix} 3-1 & 2 \\ -1 & 0-1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = 0$ $\begin{pmatrix} 2 & 2 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = 0$ $2x_1 + 2y_1 = 0$ $-x_1 - y_1 = 0$ Notice that these two equations are not independent, as the top is a multiple of the bottom one. Both give the same result: $y = -x$. This means that any vector that lies on the line $y = -x$ is an eigenvector of this matrix with eigenvalue $\lambda = 1$.	$\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = 2 \begin{pmatrix} x_2 \\ y_2 \end{pmatrix}$ $\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = 2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix}$ $\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} - 2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = 0$ $\begin{pmatrix} 3-2 & 2 \\ -1 & 0-2 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = 0$ $\begin{pmatrix} 1 & 2 \\ -1 & -2 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \end{pmatrix} = 0$ $x_2 + 2y_2 = 0$ $-x_2 - 2y_2 = 0$ Notice that these two equations are not independent, as the top is a multiple of the bottom one. Both give the same result: $y = -x/2$. This means that any vector that lies on the line $y = -x/2$ is an eigenvector of this matrix with eigenvalue $\lambda = 2$.

Figure 15.7.1 shows the lines $y=-x$ and $y=-x/2$. Any vector that lies along the line $y=-x/2$ is an eigenvector with eigenvalue $\lambda=2$, and any vector that lies along the line $y=-x$ is an eigenvector with eigenvalue $\lambda=1$. Eigenvectors that differ only in a constant factor are not treated as distinct. It is convenient and conventional to normalize the eigenvectors. Notice that we can calculate two normalized eigenvectors for each eigenvalue (pointing in one or the other direction), and the distinction between one or the other is not important.

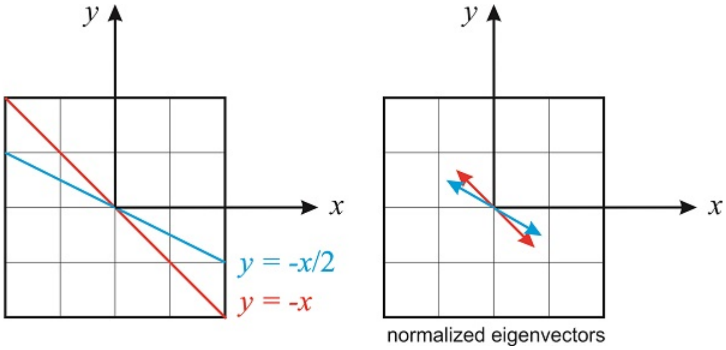

Figure 15.7.1: The eigenvectors of $\mathbf{A}$ (CC BY-NC-SA; Marcia Levitus)

In the first case, we have $y=-x$. This means that any vector of the form $\begin{pmatrix} a \\ -a \end{pmatrix}$ is an eigenvector, but we are looking for the value of a that makes this eigenvector normalized. In other words, we want $(a)^2+(-a)^2=1$, which gives $a=\pm 1/\sqrt{2}$. In conclusion, both

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \text{ and } \frac{1}{\sqrt{2}}\begin{pmatrix} -1 \\ 1 \end{pmatrix}$$

are normalized eigenvectors of

$$\mathbf{A}=\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix}$$

with eigenvalue $\lambda=1$.

For $\lambda=2$, we have that $y=-x/2$. This means that any vector of the form $\begin{pmatrix} a \\ -a/2 \end{pmatrix}$ is an eigenvector, but we are looking for the value of a that makes this eigenvector normalized. In other words, we want $(a)^2+(-a/2)^2=1$, which gives $a=\pm 2/\sqrt{5}$. In conclusion, both

$$\frac{1}{\sqrt{5}}\begin{pmatrix} 2 \\ -1 \end{pmatrix} \text{ and } \frac{1}{\sqrt{5}}\begin{pmatrix} -2 \\ 1 \end{pmatrix}$$

are normalized eigenvectors of

$$\mathbf{A}=\begin{pmatrix} 3 & 2 \\ -1 & 0 \end{pmatrix}$$

with eigenvalue $\lambda=2$.

✓ Example 15.7.2

Find the eigenvalues and nomalized eigenvectors of

$$\mathbf{M}=\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

The eigenvalues satisfy the characteristic equation:

$$\begin{vmatrix} -\lambda & 1 \\ -1 & -\lambda \end{vmatrix}=0 \rightarrow (-\lambda)(-\lambda)-(1)(-1)=\lambda^2+1=0 \rightarrow \lambda_{1,2}=\pm i$$

For $\lambda=i$:

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = i\begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$$

$$y_1 = ix_1$$

$$-x_1 = iy_1$$

Again, the two equations we get have the same information (or more formally, are linearly dependent). From either one, we get $y_1 = ix_1$.

Any vector of the form

$$\mathbf{u} = \begin{pmatrix} a \\ ia \end{pmatrix}$$

is an eigenvector of $\mathbf{M}$ with eigenvalue $\lambda = i$.

To normalize the vector (Section 14.4), we calculate the modulus of the vector using the dot product:

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u}$$

(see Section 14.2 for a discussion of the dot product of complex vectors)

$$|\mathbf{u}|^2 = \mathbf{u}^* \cdot \mathbf{u} = a^2 + (ia)(-ia) = a^2 + a^2 = 2a^2 \rightarrow |\mathbf{u}| = \pm\sqrt{2}a$$

and we divide the vector by its modulus.

The normalized eigenvectors for $\lambda = i$ are, therefore,

$$\hat{\mathbf{u}} = \pm\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix}$$

For $\lambda = -i$:

$$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \end{pmatrix} = -i\begin{pmatrix} x_1 \\ y_1 \end{pmatrix}$$

$$y_1 = -ix_1$$

$$-x_1 = -iy_1$$

From either one, we get

$$y_1 = -ix_1.$$

Any vector of the form

$$\mathbf{v} = \begin{pmatrix} a \\ -ia \end{pmatrix}$$

is an eigenvector of $\mathbf{M}$ with eigenvalue $\lambda = -i$.

To normalize the vector, we calculate the dot product:

$$|\mathbf{v}|^2 = \mathbf{v}^* \cdot \mathbf{v} = a^2 + (-ia)(ia) = a^2 + a^2 = 2a^2 \rightarrow |\mathbf{v}| = \pm\sqrt{2}a$$

The normalized eigenvectors for $\lambda = -i$ are, therefore,

$$\hat{\mathbf{v}} = \pm\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Matrix Eigenvalues: Some Important Properties

1)The eigenvalues of a triangular matrix are the diagonal elements.

$$\begin{pmatrix} a & b & c \\ 0 & d & e \\ 0 & 0 & f \end{pmatrix} \rightarrow \lambda_1 = a; \ \lambda_2 = d; \ \lambda_3 = f$$

2) If λ_1,λ_2...,λ_n, are the eigenvalues of the matrix $\mathbf{A}$, then $|\mathbf{A}| = \lambda_1 \lambda_2 \ldots \lambda_n$

3) The trace of the matrix $\mathbf{A}$ is equal to the sum of all eigenvalues of the matrix $\mathbf{A}$.

For example, for the matrix

$$\mathbf{A} = \begin{pmatrix} 1 & 1 \\ -2 & 4 \end{pmatrix} \rightarrow |\mathbf{A}| = 6 = \lambda_1 \lambda_2; \ Tr(\mathbf{A}) = 5 = \lambda_1 + \lambda_2$$

For a 2×2 matrix, the trace and the determinant are sufficient information to obtain the eigenvalues: $\lambda_1 = 2$ and $\lambda_2 = 3$.

4) Symmetric matrices-those that have a "mirror-plane" along the northeast-southwest diagonal (i.e. $\mathbf{A} = \mathbf{A}^T$) must have all real eigenvalues. Their eigenvectors are mutually orthogonal.

For example, for the matrix

$$\mathbf{A} = \begin{pmatrix} -2 & 4 & 0 \\ 4 & 1 & -1 \\ 0 & -1 & -3 \end{pmatrix}$$

the three eigenvalues are $\lambda_1 = 1 + \sqrt{21}$, $\lambda_2 = 1 - \sqrt{21}$, $\lambda_3 = -2$, and the three eigenvectors:

$$\mathbf{u}_1 = \begin{pmatrix} -5 - \sqrt{21} \\ -4 - \sqrt{21} \\ 1 \end{pmatrix}, \quad \mathbf{u}_2 = \begin{pmatrix} -5 + \sqrt{21} \\ -4 + \sqrt{21} \\ 1 \end{pmatrix}, \quad \text{and} \quad \mathbf{u}_3 = \begin{pmatrix} 1 \\ -1 \\ 1 \end{pmatrix}$$

You can prove the eigenvectors are mutually orthogonal by taking their dot products.

15.8: Hermitian Matrices

A Hermitian matrix (or self-adjoint matrix) is a square matrix with complex entries that is equal to its own conjugate transpose. In other words, $a_{ij} = a^*_{ji}$ for all entries. The elements in the diagonal need to be real, because these entries need to equal their complex conjugates: $a_{ii} = a^*_{ii}$:

$$\begin{pmatrix} a & b+ci & d+ei \\ b-ci & f & g+hi \\ d-ei & g-hi & j \end{pmatrix}$$

where all the symbols in this matrix except for i represent real numbers.

Hermitian matrices are a generalization of the symmetric real matrices we just talked about, and they also have real eigenvalues, and eigenvectors that form a mutually orthogonal set.

> Need help? The link below contains solved examples:
>
> - An example from a midterm: Eigenvectors, Eigenvalues, Inverse, Orthogonality, Hermitiannon Hermitian http://tinyurl.com/n38938e

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15.9: Problems

? Problem 15.9.1

Given

$$\mathbf{A}=\begin{pmatrix}2&3&-1\\-5&0&6\\0&2&3\end{pmatrix};\mathbf{B}=\begin{pmatrix}2\\1\\0\end{pmatrix};\mathbf{C}=\begin{pmatrix}0&1\\2&0\\-1&3\end{pmatrix}$$

Multiply all possible pairs of matrices.

? Problem 15.9.2

The matrix representation of a spin $1/2$ system was introduced by Pauli in 1926. The Pauli spin matrices are the matrix representation of the angular momentum operator for a single spin $1/2$ system and are defined as:

$$\sigma_{\mathbf{x}}=\begin{pmatrix}0&1\\1&0\end{pmatrix};\sigma_{\mathbf{y}}=\begin{pmatrix}0&-i\\i&0\end{pmatrix};\sigma_{\mathbf{z}}=\begin{pmatrix}1&0\\0&-1\end{pmatrix}$$

1. Show that $\sigma_{\mathbf{x}}\sigma_{\mathbf{y}}=i\sigma_{\mathbf{z}}$, $\sigma_{\mathbf{y}}\sigma_{\mathbf{z}}=i\sigma_{\mathbf{x}}$ and $\sigma_{\mathbf{z}}\sigma_{\mathbf{x}}=i\sigma_{\mathbf{y}}$
2. Calculate the commutator $[\sigma_{\mathbf{x}},\sigma_{\mathbf{y}}]$.
3. Show that ${\sigma_{\mathbf{x}}}^2={\sigma_{\mathbf{y}}}^2={\sigma_{\mathbf{z}}}^2=\mathbf{I}$, where $\mathbf{I}$ is the identity matrix. Hint: as with numbers, the square of a matrix is the matrix multiplied by itself.

? Problem 15.9.3

The inversion operator, $\hat{i}$ transforms the point (x,y,z) into $(-x,-y,-z)$. Write down the matrix that corresponds to this operator.

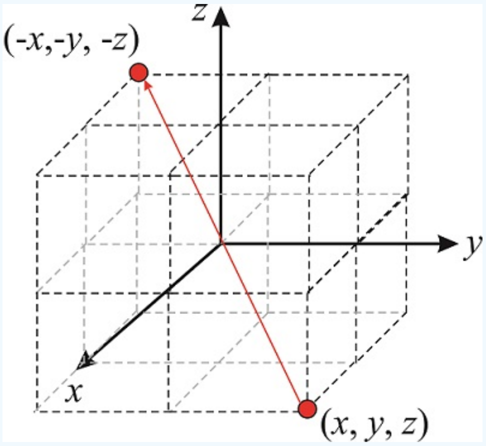

Figure 15.9.1: The inversion operator (CC BY-NC-SA; Marcia Levitus)

? Problem 15.9.4

Calculate the inverse of $\mathbf{A}$ by definition.

$$\mathbf{A}=\begin{pmatrix}1&-2\\0&1\end{pmatrix}$$

Problem 15.9.5

Calculate the inverse of $\mathbf{A}$ by definition.

$$\mathbf{A}=\begin{pmatrix}\cos\theta & -\sin\theta\\ \sin\theta & \cos\theta\end{pmatrix}$$

Problem 15.9.6

Find the eigenvalues and nomalized eigenvectors of

$$\mathbf{M_1}=\begin{pmatrix}2 & 0\\ 0 & -3\end{pmatrix}$$

$$\mathbf{M_2}=\begin{pmatrix}1 & 1+i\\ 1-i & 1\end{pmatrix}$$

Problem 15.9.7

Given,

$$\mathbf{M_3}=\begin{pmatrix}1 & 1-i\\ 1+i & 1\end{pmatrix}$$

1. Show that the matrix is Hermitian.
2. Calculate the eigenvectors and prove they are orthogonal.

CHAPTER OVERVIEW

16: Formula Sheets

16.1: Some Important Numbers

$$\ln 2 \approx 0.69$$
$$e \approx 2.72$$
$$e^{-1} \approx 0.37$$

16.2: Quadratic Equation

$$ax^2 + bx + c = 0 \rightarrow x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

16.3: Logarithms and Exponentials

- $\log_b xy = \log_b x + \log_b y$
- $\log_b x^y = y \log_b x$
- $\log_b 1 = 0$
- $\log_b (1/x) = -\log_b x$
- $e^{x+y} = e^x e^y$
- $e^{x-y} = e^x / e^y$

16.4: Trigonometric Identities

- $\sin^2 u+\cos^2 u=1$
- $\tan u=\frac{\sin u}{\cos u}$
- $\sin\left(\frac{\pi}{2}-u\right)=\cos u$
- $\cos\left(\frac{\pi}{2}-u\right)=\sin u$
- $\sin(u\pm v)=\sin u\cos v\pm\cos u\sin v$
- $\cos(u\pm v)=\cos u\cos v\mp\sin u\sin v$
- $\sin(-u)=-\sin u$
- $\cos(-u)=\cos u$
- $\tan(-u)=-\tan u$
- $\sin u\cos v=\frac{1}{2}[\sin(u+v)+\sin(u-v)]$
- $\sin u\sin v=\frac{1}{2}[\cos(u-v)-\cos(u+v)]$
- $\cos u\cos v=\frac{1}{2}[\cos(u-v)+\cos(u+v)]$

16.5: Complex Numbers

$$re^{\pm i\phi} = r\cos\phi \pm ir\sin\phi = x \pm iy$$

16.6: Operators

$$[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

$$[\hat{A},\hat{B}] = 0 \text{ if the operators } \hat{A} \text{ and } \hat{B} \text{ commute.}$$

16.7: Taylor Series

$$f(x) = a_0 + a_1(x-h) + a_2(x-h)^2 + a_3(x-h)^3 + \dots$$

$$a_n = \frac{1}{n!}\left(\frac{d^n f(x)}{dx^n}\right)_h, n = 1, 2, 3 \dots$$

16.8: Fourier Series

For a periodic function of period $2L$:

$$f(x)=\frac{a_0}{2}+\sum_{n=1}^{\infty}a_n\cos\left(\frac{n\pi x}{L}\right)+\sum_{n=1}^{\infty}b_n\sin\left(\frac{n\pi x}{L}\right)$$

$$a_0=\frac{1}{L}\int_{-L}^{L}f(x)dx$$

$$a_n=\frac{1}{L}\int_{-L}^{L}f(x)\cos\left(\frac{n\pi x}{L}\right)dx$$

$$b_n=\frac{1}{L}\int_{-L}^{L}f(x)\sin\left(\frac{n\pi x}{L}\right)dx$$

16.9: Derivatives and Primitives (Indefinite Integrals)

$f(x)$	$f'(x)$	$\int f(x)dx(\pm c)$
k	0	kx
x^n	$nx^{n-1}, n \neq 0$	$\frac{x^{n+1}}{n+1}, n \neq -1$
$\frac{1}{x}$	$-\frac{1}{x^2}$	$ln\|x\|$
a^x	$a^x \ln a$	$\frac{a^x}{\ln a}$
e^x	e^x	e^x
$\log_a x$	$\frac{1}{x \ln a}$	$\frac{x \ln x - x}{\ln a}$
$\ln x$	$\frac{1}{x}$	$x \ln x - x$
$\sin x$	$\cos x$	$-\cos x$
$\cos x$	$-\sin x$	$\sin x$
$\tan x$	$\frac{1}{\cos^2 x}$	$-\ln(\cos x)$
$\arcsin x$	$\frac{1}{\sqrt{1-x^2}}$	$x \arcsin x + \sqrt{1-x^2}$
$\arccos x$	$-\frac{1}{\sqrt{1-x^2}}$	$x \arccos x - \sqrt{1-x^2}$
$\arctan x$	$\frac{1}{1+x^2}$	$x \arctan x - \frac{1}{2}\ln(1+x^2)$
$\frac{1}{a^2+x^2}$	$\frac{-2x}{(a^2+x^2)^2}$	$\frac{1}{a}\arctan\left(\frac{x}{a}\right)$
$\frac{1}{\sqrt{a^2-x^2}}$	$\frac{x}{(a^2-x^2)^{\frac{3}{2}}}$	$\arcsin\left(\frac{x}{a}\right)$

- $\int \sin^2(ax)dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} + c$
- $\int \cos^2(ax)dx = \frac{x}{2} + \frac{\sin(2ax)}{4a} + c$
- $\int \sin^3(ax)dx = \frac{1}{12a}\cos(3ax) - \frac{3}{4a}\cos(ax) + c$
- $\int \cos^3(ax)dx = \frac{1}{12a}\sin(3ax) + \frac{3}{4a}\sin(ax) + c$
- $\int x\cos(ax)dx = \frac{\cos(ax)}{a^2} + \frac{\sin(ax)}{a}x + c$
- $\int x\sin(ax)dx = \frac{\sin(ax)}{a^2} - \frac{\cos(ax)}{a}x + c$
- $\int x\sin^2(ax)dx = \frac{x^2}{4} - \frac{x\sin(2ax)}{4a} - \frac{\cos(2ax)}{8a^2} + c$
- $\int xe^{x^2}dx = e^{x^2}/2 + c$
- $\int xe^{ax} = \frac{e^{ax}(ax-1)}{a^2} + c$
- $\int \frac{x}{x^2+1}dx = \frac{1}{2}\ln(1+x^2) + c$

16.10: Definite integrals

- $\int_0^\infty xe^{-x^2}dx = \frac{1}{2}$
- $\int_0^\infty e^{-ax}dx = \frac{1}{a}, a > 0$
- $\int_0^\infty \sqrt{x}e^{-ax}dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$
- $\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}}, a > 0$
- $\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{1.3.5\ldots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$
- $\int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$, $a > 0$, n positive integer

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16.11: Differentiation Rules

- $\frac{d[f(x)+g(x)]}{dx} = \frac{df(x)}{dx} + \frac{dg(x)}{dx}$
- $\frac{d[f(x)g(x)]}{dx} = f(x)\frac{dg(x)}{dx} + g(x)\frac{df(x)}{dx}$
- $\frac{d[af(x)]}{dx} = a\frac{df(x)}{dx}$
- $\frac{df(g(x))}{dx} = \frac{df(g)}{dg}\frac{dg(x)}{dx}$

16.12: Partial Derivatives

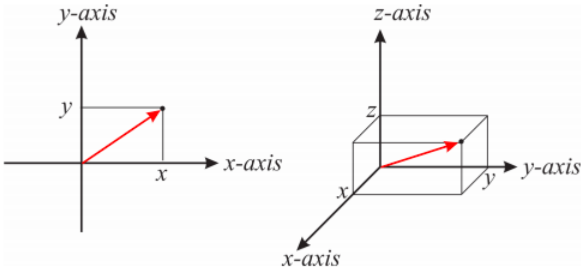
- $\frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$
- $\left(\frac{\partial y}{\partial x}\right)_{z,u} = \frac{1}{(\partial x/\partial y)_{z,u}}$
- $\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$
- $du = \left(\frac{\partial u}{\partial x_1}\right)_{x_2,x_3\ldots} dx_1 + \left(\frac{\partial u}{\partial x_2}\right)_{x_1,x_3\ldots} dx_2 + \left(\frac{\partial u}{\partial x_3}\right)_{x_1,x_2\ldots} dx_3$
- Given $u = u(x, y)$, $x = x(\theta, r)$ and $y = y(\theta, r)$

$$\left(\frac{\partial u}{\partial r}\right)_\theta = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial r}\right)_\theta + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial r}\right)_\theta$$

$$\left(\frac{\partial u}{\partial \theta}\right)_r = \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial x}{\partial \theta}\right)_r + \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial y}{\partial \theta}\right)_r$$

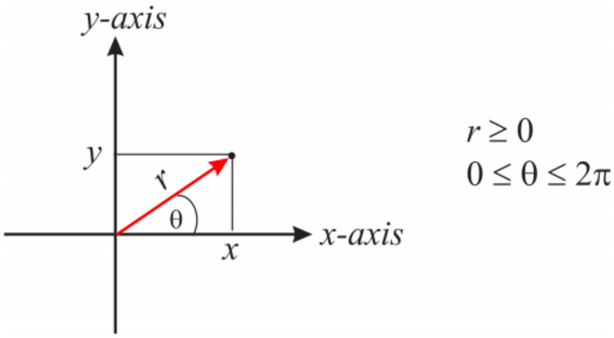
16.13: Coordinate Systems

Cartesian coordinates



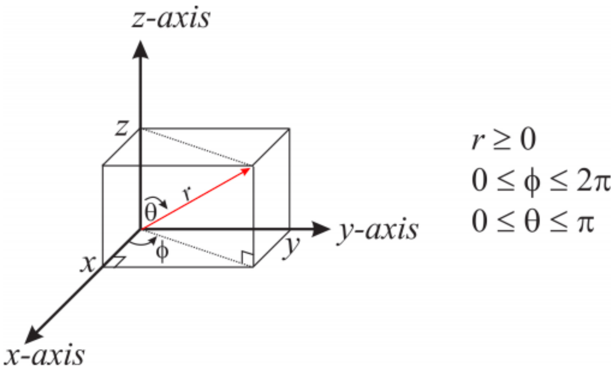
2 dimensions: area element: $dA = dx.dy$.
3 dimensions: volume element: $dV = dx.dy.dz$.

Polar coordinates



- $x = r\cos\theta$
- $y = r\sin\theta$
- $r^2 = x^2 + y^2$
- $tan\theta = y/x$
- $dA = r.dr.d\theta$

Spherical coordinates



- $x = r\sin\theta\cos\phi$
- $y = r\sin\theta\sin\phi$
- $z = r\cos\theta$
- $r^2 = x^2 + y^2 + z^2$

- $\theta = \cos^{-1}\left[\frac{z}{\sqrt{x^2+y^2+z^2}}\right]$
- $\phi = \tan^{-1}\left(\frac{y}{x}\right)$
- $dV = r^2 \sin\theta dr.\, d\phi.\, d\theta$

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Glossary

Sample Word 1 | Sample Definition 1

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