Applied Mathematics for Chemists II

Vector fields, partial differentiation, cylindrical and spherical coordinates, multiple integrals, line integrals, the wave and the Schrödinger equations, separation of variables method. Inner Product Spaces. Fourier Series.

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Part V

Further Topics in Linear Algebra

1

Complex Functions and Transformations

1 Introduction

When we ended the prequel with linear algebra, we found the complex number system to be highly useful in many ways. We'll want to keep this in mind as we progress into further topics in the field of linear algebra. Instead of dealing with transformations of finite dimensional vector spaces like $\mathbb{R}^n$ and $\mathbb{C}^n$, we will care about the spaces of functions on these spaces. So we find ourselves studying a bit of a nested structure.

Spaces of functions are of great importance. In studying these spaces, we find ways to solve problems we will approach in the future (e.g., partial differential equations). These spaces are, in some sense, infinite dimensional which means we can no longer draw pictures that accurately describe what is occuring. Luckily enough, the intuition gained from the finite dimensional case will work just fine.

We begin with complex functions as they are immensely fundamental in the study of the physical world and our mathematical development. Once we have covered this area, we can adjust our view to the relevant spaces of functions that arise in areas such as quantum mechanics and partial differential equations in general. As we did in the finite dimensional case, we can consider how these linear spaces transform under linear operators. Finally, we make a nudge towards the spectral theory (eigenvalues and eigenvectors) via Fourier theory.

2 Complex Functions

In the prequel, we studied in depth single variable real valued functions $f\colon \mathbb{R} \to \mathbb{R}$. That is, functions with a single real variable as an input that outputs a single real number. Analogously, a ***complex function*** is a function, $f\colon \mathbb{C} \to \mathbb{C}$, with a complex number given as input and a complex number output as well. The interesting quality to note is that we specified a

complex number $z \in \mathbb{C}$ by putting

$$z = x + iy,$$

which means that single complex number is defined by two real numbers. Recall as well that we could write a complex number in polar form

$$z = re^{i\theta},$$

which again requires the specification of two real numbers. All of this is to say that we are allowed to (when it is helpful) think of complex functions as functions that input two real numbers $x, y \in \mathbb{R}$ and outputs two real numbers. Hence we would write $f : \mathbb{R}^2 \to \mathbb{R}^2$. The additional structure with complex numbers (in how we multiply them) forces us to think of $f : \mathbb{C} \to \mathbb{C}$ in a slightly different manner than their real valued counterparts which is why we cannot always make this identification!

2.1 Cartesian and Polar Representations

Consider a complex function $f : \mathbb{C} \to \mathbb{C}$. Then, as always, we define this function by providing an output for each input and specify this by

$$f(z) = w,$$

where both $w \in \mathbb{C}$ and $z \in \mathbb{C}$ are complex numbers. Hence, we can further decompose this function by writing

$$f(z) = u(z) + iv(z),$$

where $u(z)$ and $v(z)$ are real valued functions $u, v : \mathbb{C} \to \mathbb{R}$. This decomposition is rather helpful in providing us a way to visualize the complex function f. In this case, we are seeing what happens to the real $u(z)$ and imaginary part $v(z)$ of the output as we vary the complex input.

Of course, we can also write

$$f(z) = r(z)e^{i\theta(z)},$$

where again $r, \theta : \mathbb{C} \to \mathbb{R}$. In this perspective, we are seeing what happens to the argument $\theta(z)$ and modulus $r(z)$ as we vary the complex input. Which way of decomposing f we choose is typically decided on the situation at hand. It has more to do with the symmetry of the function than anything else! In this polar representation of the function, we refer to $\theta(z)$ as a ***phase***.

Examples of functions and some visualizations (vec fields and what not)

2.2 Complex Valued Functions

A major focus in this course is understanding the mathematics behind quantum mechanics. For a chemist, this knowledge is rather important since modern theory is mostly quantum in nature. What isn't quantum is likely thermodynamical or electrodynamical in nature and we will get to these topics a bit later on.

Recall that wavefunctions are solutions to Schrödinger's equation. In the broadest generality, wavefunctions are functions that are complex valued and whose domain of definition is on some region Ω in space $\mathbb{R}^3$. More generally, we can allow for Ω to a be a region in other spaces as well. To restate this, we are considering a function of the form $\Psi : \Omega \to \mathbb{C}$ where we will specify what the domain Ω is. Previously, we looked at models in lower dimensions (e.g.,

the free particle in the 1-dimensional box) since we have yet to properly discuss multivariate functions.

For now, consider a complex function $\Psi\colon [a,b] \to \mathbb{C}$ that has a single real variable as an input. Thus, we define this function by $\Psi(x) = z$, where $z \in \mathbb{C}$. Of course, we get the Cartesian decomposition

$$\Psi(x) = u(x) + i\,v(x),$$

or the polar decomposition

$$\Psi(x) = r(x)e^{i\theta(x)}.$$

The great thing in this case is that we can differentiate and integrate wavefunctions in a way that's no different than single variable real functions! Fundamentally, this is due to the fact that our understanding of the derivative has only been defined for a single real value input. We will deepen our understanding later. So, for a wavefunction we have that

$$\Psi'(x) = u'(x) + i\,v'(x),$$

and in the polar case we have

$$\Psi'(x) = r'(x)e^{i\theta(x)} + r(x)e^{i\theta(x)}\theta'(x),$$

which follows from the chain rule.

Exercise 2.1. Verify the polar derivative above is correct.

Integration follows the fundamental theorem of calculus and hence we have

$$\int_a^b \Psi'(x)\,dx = \Psi(b) - \Psi(a).$$

So, for example, in the cartesian representation we have

$$\int_a^b \Psi'(x)\,dx = \int_a^b u'(x)\,dx + i\int_a^b v'(x)\,dx = [u(b) - u(a)] + i[v(b) - v(a)].$$

Remark 2.1. Complex functions (i.e., functions with complex valued inputs) have different behavior with integration and differentiation which we will not discuss at all. The closest we will get to this structure is calculus in $\mathbb{R}^2$.

Example 2.1: Wavefunctions in the Box

Let $\Omega = [0, L]$ and recall that the normalized states of the particle in the 1-dimensional box were given by

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

Recall as well that we could write a wavefunction as a superposition of states by

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

Though these states are real valued, there is no physics that requires this. Similarly, the coefficients a_n are also not constrained to be real valued constants either. In the

broadest generality, Ψ can be a complex valued function and the coefficients a_n can be complex as well.
Fundamentally, this is due to the physical understanding of the solutions to Schrödinger's equation. When we are looking for physically meaningful interpretations of a wavefunction, we must evaluate an integral. We can think of this act of integration as performing a measurement. For example, let $[a,b]$ be a subinterval of $[0,L]$, then we can compute the probability of the particle with wavefunction $\Psi(x)$ to be in the region $[a,b]$ by

$$P_{[a,b]}(\Psi) = \int_a^b \|\Psi(x)\|^2 dx,$$

where we have the pointwise modulus of the complex valued function

$$\|\Psi(x)\|^2 = \Psi^*(x)\Psi(x),$$

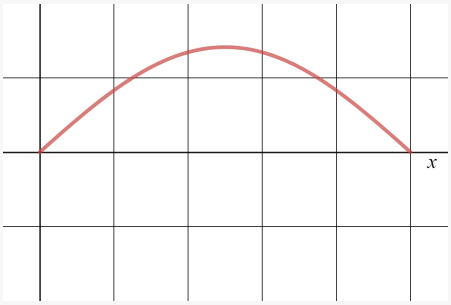
where * indicates the complex conjugate. Say we take the cartesian representation for $\Psi(x)$ by $\Psi(x) = u(x) + i\,v(x)$, then

$$\|\Psi(x)\|^2 = u^2(x) + v^2(x).$$

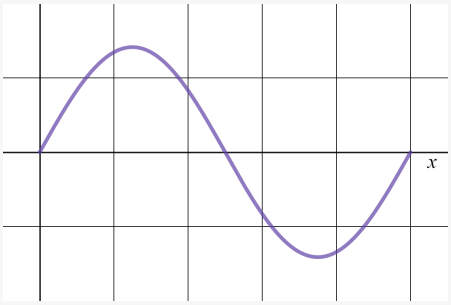
Let $\Psi(x) = \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x)$ be a superposition state. We can compute the probability that the particle is in the first half of the region $[0,L]$ by computing

$$\begin{aligned}
P_{[0,L/2]}(\Psi) &= \int_0^{L/2} \|\Psi(x)\|^2 dx \\
&= \int_0^{L/2} \frac{1}{2}\psi_1^2(x) + \psi_1(x)\psi_2(x) + \frac{1}{2}\psi_2^2(x) dx \\
&= \int_0^{L/2} \frac{1}{2}\left(\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\right)^2 + \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right) + \frac{1}{2}\left(\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)\right)^2 dx \\
&= \frac{1}{2} + \frac{4}{3\pi} \\
&\approx .924.
\end{aligned}$$

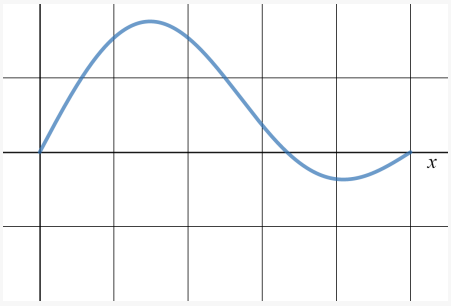
Through this calculation we have found that the probability that the particle is the first half of box is about 92.5%. Since the particle must be in the box, it follows that the probability of the particle being in $[L/2, L]$ must be $1 - \frac{1}{2} - \frac{4}{3\pi}$ or roughly 7.5%. This is quite different than we would expect classically!
We can plot the functions used above to see why this is the case.



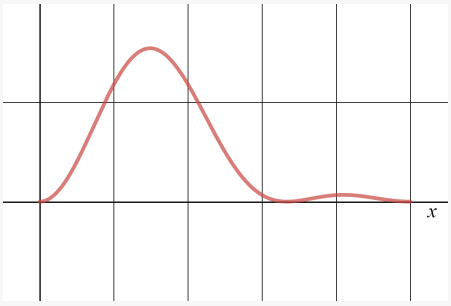
(a) Normalized state $\psi_1(x)$.



(b) Normalized state $\psi_2(x)$.



(c) The wavefunction $\Psi(x)$.



(d) The probability function $\|\Psi(x)\|^2$.

The plots above of course show us that the integration makes sense. We can see in (d) that the function that describes the probability is heavily weighted towards the first half of the interval $[0, L]$. One may then wonder if this is always true? That is, if I were to check back later in time, is the probability still distributed in the same way? The answer is no. Later, we will introduce the time dependent version of the Schrödinger equation where we will see that these wavefunctions also evolve over time. To some extent, we can see a bit of this behavior now.

If we instead change our wavefunction by introducing a phase difference for each of the components. What will happen in this case? If you have seen the double slit experiment, you may guess that introducing a phase difference can change the result (as phase difference causes interference). Instead of the $\Psi(x)$ above, take

$$\tilde{\Psi}(x) = \frac{e^{i\theta}}{\sqrt{2}}\psi_1(x) + \frac{e^{i\phi}}{\sqrt{2}}\psi_2(x).$$

In this case, all we have done is made the wavefunction complex. If, however, we consider the probability distribution given by this new wave function, we find

$$\|\tilde{\Psi}(x)\|^2 = \tilde{\Psi}^*(x)\tilde{\Psi}(x) = \frac{1}{2}\psi_1^2(x) + \frac{e^{i(\theta-\phi)}}{2}\psi_1(x)\psi_2(x) + \frac{e^{i(\phi-\theta)}}{2}\psi_1(x)\psi_2(x) + \frac{1}{2}\psi_2^2(x).$$

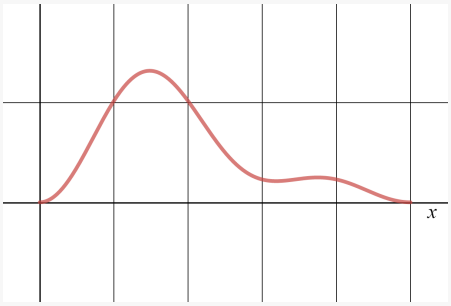
This is now slightly different! However, we can note that

$$\frac{e^{i(\theta-\phi)} + e^{i(\phi-\theta)}}{2} = \cos(\theta-\phi),$$

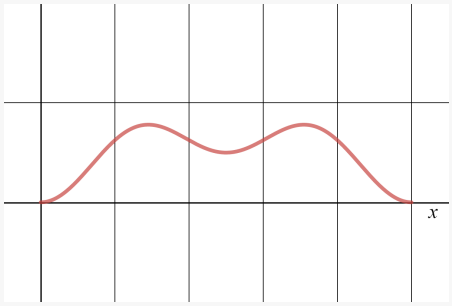
and hence we have

$$\|\tilde{\Psi}(x)\|^2 = \tilde{\Psi}^*(x)\tilde{\Psi}(x) = \frac{1}{2}\psi_1^2(x) + \cos(\theta-\phi)\psi_1(x)\psi_2(x) + \frac{1}{2}\psi_2^2(x).$$

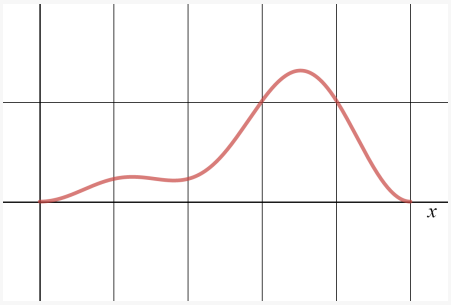
So the phase difference $\delta = |\theta - \phi|$ between the two states causes the wavefunction to change. In the first example with $\Psi(x)$, the phase difference $\delta = 0$ and we observed the probability function $\|\Psi(x)\|^2$. However, let us see what happens as we change the phase.



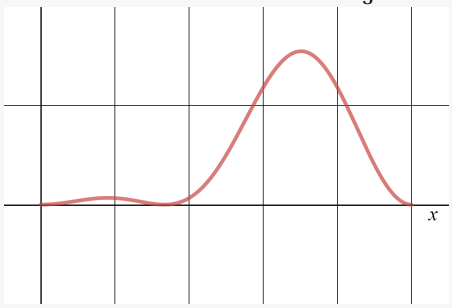
(a) Phase difference $\delta = 0$.



(b) Phase difference $\delta = \frac{\pi}{3}$.



(c) Phase difference $\delta = \frac{2\pi}{3}$.



(d) Phase difference $\delta = \pi$.

Interestingly enough, it seems that the phase difference “moves" the particle around in the box. Of course, the particle itself is not moving, but the function that represents the likelihood of its position changes as the phase changes. The largest difference in phase is π, and when we see this, we find that the distribution given by $\|\tilde{\Psi}(x)\|^2$ is the mirror image of the original $\|\Psi(x)\|^2$.
There are two important remarks to note here.

1. We can change the global phase of the system without changing the probability of measurement. That is, $e^{i\theta}\Psi(x)$ has no discernable difference from $\Psi(x)$ (you can verify this from the work above).

2. This difference in phase seems to drive some form of motion for a particle. It is with this insight that we will later revisit the time dependent version of the Schrödinger equation and see how the time component relates to phase.

Remark 2.2. In a sense, the integral defined above $P_{[a,b]}(\Psi)$ is a real valued function with a function as an input. Though we have not noted this until now, it becomes important in the future.

All of this is to say that we must be able to work with complex valued functions. They show up in physics and help us describe what we observe through nature. It's important to remember that all measurements we make in a lab must be real valued, and so our mathematical models for these measurements must take that into account as well.

2 Hilbert Spaces

1 Introduction

Recall the importance of the dot product in space. Given two vectors $\vec{u}, \vec{v} \in \mathbb{R}^3$, we defined the dot product by

$$\vec{u} \cdot \vec{v} = u_1 v_1 + u_2 v_2 + u_3 v_3,$$

and we also referred to this as an inner product. The dot product allowed us to project a vector onto its components by, for example,

$$\vec{u} \cdot \hat{x} = u_1.$$

This was extremely useful for us. On top of that, the dot product provided us a means of computing the length of a vector by putting

$$\|\vec{u}\| = \sqrt{\vec{u} \cdot \vec{u}}.$$

Underlying much of the theory of space was this structure.

Later, we introduced the Hermitian inner product on complex vectors. As it turns out, this inner product is strictly more general than the dot product. If we had two vectors $\vec{a}, \vec{b} \in \mathbb{C}^n$ (i.e., vectors with n complex number entries) then we defined the inner product by

$$\langle \vec{a}, \vec{b} \rangle = \sum_{j=1}^{n} a_j b_j^*.$$

Note that if $\vec{a}$ and $\vec{b}$ only have real entries, then the complex conjugate $b_j^* = b_j$ and we are left with the typical dot product for $\mathbb{R}^n$. It suffices to say, that we need only care about this Hermitian inner product. In the same vein, we receive all the wonderful benefits of the dot

product. For example, we can project a vector by taking

$$\hat{\boldsymbol{x}}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

and computing

$$\langle \vec{\boldsymbol{a}}, \vec{\boldsymbol{x}}_1 \rangle = a_1.$$

Likewise, the length of a complex vector is given by

$$\| \vec{\boldsymbol{a}} \| = \sqrt{\langle \vec{\boldsymbol{a}}, \vec{\boldsymbol{a}} \rangle}.$$

Nothing is lost from this more general approach, and this more general approach extends far beyond finite dimensional complex vectors!

1.1 Infinite Dimensions

The dimension of a vector is the number of entries needed to fully describe the vector. From the examples before, we can say that the vectors $\vec{\boldsymbol{u}}, \vec{\boldsymbol{v}} \in \mathbb{R}^3$ are 3-dimensional real vectors and the vectors $\vec{\boldsymbol{a}}, \vec{\boldsymbol{b}} \in \mathbb{C}^n$ are n-dimensional complex vectors. There is no restriction on the size of n, and n can in fact be infinite!

This section of the text is primarily concerned with extending our linear algebra techniques to the infinite dimensional case. Though this may sound ominous, it simply builds upon what we already know. In essence, we will combine our knowledge of functions, infinite series, integrals, and linear algebra to complete the theory for infinite dimensions. Put simply, functions will play the role of vectors while series and integrals will play the role of inner products. This viewpoint places us viewing mathematics from the top, where we can always reduce the general story to something more specific when need be. Ultimately, this allows one to understand one general structure instead of many individual ones.

2 Inner Products

Before we define general inner products, let us recall the definition of a vector space. In the prequel, we had that a vector space V over some field $\mathbb{F}$ (the numbers we choose as entries) is a set containing vectors that satisfy eight different properties.

Exercise 2.1. Find the definition in the previous text and review it.

Definition 2.1: Inner Product

An ***inner product*** on a vector space V over a field $\mathbb{F}$ is a bilinear (sometimes sesquilinear) function

$$\langle \cdot, \cdot \rangle : V \times V \to \mathbb{F},$$

that satisfies

i. (Nondegenerate) For a $\vec{\boldsymbol{a}} \in V$ we have that $\langle \vec{\boldsymbol{a}}, \vec{\boldsymbol{a}} \rangle = 0$ if and only if $\vec{\boldsymbol{a}} = \vec{\boldsymbol{0}}$;

ii. (Positive definite) For any nonzero $\vec{a} \in V$ we have that $\langle \vec{a}, \vec{a} \rangle > 0$;

iii. (Symmetric) For any $\vec{a}, \vec{b} \in V$ we have that $\left\langle \vec{a}, \vec{b} \right\rangle = \left\langle \vec{b}, \vec{a} \right\rangle$.

What we are denoting is a function $\langle \cdot, \cdot \rangle$ that has two vectors ($V \times V$) as inputs where see $\cdot$ and outputs some number in the designated field $\mathbb{F}$. When we say bilinear, we mean that the function is linear in each input. For example, we have for vectors $\vec{a}, \vec{b}, \vec{c} \in V$ and a scalar $\alpha \in \mathbb{F}$ that

$$\left\langle \alpha \vec{a} + \vec{b}, \vec{c} \right\rangle = \alpha \langle \vec{a}, \vec{c} \rangle + \left\langle \vec{b}, \vec{c} \right\rangle,$$

which shows the linearity in the first input. The second input is linear as well.
Similarly, if the field $\mathbb{F} = \mathbb{C}$, then the inner product need be sesquilinear in that we instead have the addition of a complex conjugate in the second position. That is, let $\alpha, \beta \in \mathbb{C}$ and we have

$$\left\langle \alpha \vec{a} + \vec{b}, \beta \vec{c} \right\rangle = \alpha \beta^* \langle \vec{a}, \vec{c} \rangle + \beta^* \left\langle \vec{b}, \vec{c} \right\rangle.$$

The first position is simply linear.

3

Linear Operators

4

Fourier Theory

spectral theory with fourier and with 1st and second order derivatives and matices. different domains for different spectra, schrodinger equation with quadratic potential QHO. Start with complex functions since they introduce multivariate functions and inner products nicely. Can talk about U(1)?

Part VI

Calculus in Higher Dimensions

5

Curves and Fields

1 Overview of multivariate functions

Now that we have covered enough of the complex numbers, we will move back into the vector space $\mathbb{R}^n$ and analyze the types of functions we can have with this space. Specifically, we will concentrate on $\mathbb{R}^3$ (or $\mathbb{R}^2$) and functions of the form:

$$\gamma\colon \mathbb{R} \to \mathbb{R}^3 \tag{Eq. 5.1.1}$$

$$f\colon \mathbb{R}^3 \to \mathbb{R} \tag{Eq. 5.1.2}$$

$$\mathbf{v}\colon \mathbb{R}^3 \to \mathbb{R}^3. \tag{Eq. 5.1.3}$$

Abstractly, I could call each one of these functions a *field* (in the physics sense). However, I'll refrain from this (and let the mathematicians breathe a sigh of relief).

6

Differential and Integration Operators

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Coordinate Systems and Parameterization

Part VII

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Fourier Transforms and Harmonics