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Nonlinear Spectroscopy
Fundamentals and Applications

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Preface

This text is a work in progress and was last updated on September 7, 2022. Please send comments or corrections to nonlinearspec@gmail.com.

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Chapter 1

Introduction

1.1   Fundamental Concepts

Spectroscopy is the study of interactions between light and matter. In many cases, the objective of a spectroscopic experiment is to learn something about the material system involved, as when a chemist measures the infrared spectrum of a new compound to characterize its structure. In others, the electromagnetic field itself is the essential quantity, as in the passage of high-speed internet signal through fiber-optic cables. In all cases, however, understanding a spectroscopic measurement requires a knowledge of three things: the electromagnetic field, the material system, and the physical interactions between them.

For most of us, the basic properties of matter are comparatively intuitive, due both to direct experience (we can feel, touch, and see matter) and to education. (Most of undergraduate chemistry and much of undergraduate physics are devoted to learning about the properties of material systems.) Although the quantum-mechanical rules governing matter at the molecular scale may not always be intuitive, for most purposes we can ignore the difficult concepts and think in terms of intuitive classical models such as ball-and-spring descriptions of molecular mechanics.

In contrast, the electromagnetic (EM) field can often feel abstract and unfamiliar. Although we can indeed see light and feel its warmth, these direct experiences offer little intuition about its microscopic properties. Moreover, the vector calculus inherent in Maxwell's equations (the fundamental equations of the electromagnetic field) constitutes a roadblock to many beginning students even in mathematically-inclined sciences such as physics and chemistry.

Although experience and hard work are the only tools that can entirely overcome these barriers, it is helpful to build a basic conceptual picture of what the electromagnetic field is and how it behaves *before* embarking on a rigorous mathematical study. This is the focus of the current chapter.

1.2   What *is* a field anyway?

Perhaps the most fundamental conceptual difficulty in electrodynamics is answering the simple question: What exactly *is* the electromagnetic field?

Like many ontological questions in science, the question defies a simple answer. Indeed, any answer we provide will ultimately lead us to further difficult questions; for example, "What is charge?", "What is mass?", "What is gravity?", or even "What is energy?" Such questions are difficult to answer concretely since they ask us to quantify in more basic terms entities that seem fundamental to the world around us. Fortunately, science is an empirical project and it suffices for our purpose to define abstract quantities by their effects in the physical world. Mass, for example, may be a difficult quantity to define abstractly, but it is easy to identify in practice: mass, we might say, is the stuff that makes objects heavy. Gravity, likewise, may appear obscure as an abstract concept, but we readily understand its physical significance when we drop a cup of coffee.

In the same way, the electromagnetic field is an abstract quantity that (like mass, charge, or gravity) we postulate to exist in order to explain the behavior of the world around us. In short, although it may be difficult to quantify physically what the electromagnetic field *is*, we can certainly describe physically what it *does*. In fact, the analogy between the electromagnetic field and the gravitational field proves to be a surprisingly useful one. Just as the gravitational field is what causes massive objects to interact, the electromagnetic field is what causes charged objects to interact. Just as the mass of an object defines the strength of its gravitational interactions with other objects, the charge of an object defines the strength of its electromagnetic interactions.

At a conceptual level, this description is perhaps the most fundamental answer we can provide to our original question: *the electromagnetic field is the physical quantity that mediates interactions between charged particles.*

1.2.1   The field as a force map

To be more precise, the electromagnetic field is in fact a composite of two distinct but closely related quantities – the electric field and the magnetic field. Together, these two quantities determine both the electric and magnetic forces that are so central to the dynamics of charged particles. Unlike mass or charge, however, the electric and magnetic fields are properties of an entire physical system and cannot be attributed to individual particles or groups of particles. In fact, although we sometimes speak informally of the field produced by a single particle or component of a system, in the end only the total field has physical meaning. In principle, there is a single electromagnetic field that describes the entire universe!

As one might expect, any physically-informative quantity that describes the state of an entire universe must encode a tremendous amount of information. The electromagnetic field accomplishes this task by varying its value as a function of position in space. In fact, this is exactly what the term "field" means in the context of mathematical physics: a *field* is simply a function of three-dimensional space. In a very real sense, the electric and magnetic

fields may thus be considered as special kinds of "maps" of the universe; their values at a given point in space tell us about the forces that would be experienced by a charged particle at that location. Since the force felt by a particle is a vector quantity (i.e. it has distinct components along the three spatial axes x, y, and z), the electric and magnetic fields are likewise *vector fields*, i.e. their values at any given point in space are vector quantities. More specifically:

- The electric field $e(r)$ is proportional to the force that would be experienced by a very small *stationary* particle with a very small charge at the location r in space.

- The magnetic field $b(r)$ describes the *additional* force (i.e., in addition to the force from the electric field) that would be experienced by a very small *moving* particle with a very small charge at a given position r in space.

If the repeated use of the phrase "very small" seems rather vague here, you're absolutely right. The force law stated here is in fact an approximation that studiously avoids the mathematical complications inherent in a rigorous treatment. Although this approximate expression will be sufficient for all applications in this course, Section 1.4 gives a brief explanation of exactly what complications we're avoiding and how they could be handled rigorously.

Mathematically, these two statements are embedded in a fundamental equation known as the *Lorentz Force Law*:

$$F_{\text{EM}} \approx qe(r, t) + \frac{q}{c}v \times b(r, t). \tag{1.1}$$

Here F_{EM} represents the electromagnetic force experienced by a particle of charge q located at the position r and moving with a velocity v, and c is the speed of light.[1] The symbol $\times$ is a vector cross product, indicating that the magnetic force is perpendicular both to the orientation of the magnetic field and to the particle velocity. In contrast, the force exerted by the electric field is independent of velocity and is always parallel to the electric field. Our use of the approximation symbol "$\approx$" rather than equality "$=$" is a nod to the "very small" approximations mentioned above (see Section 1.4).

Two points are worth emphasizing here. First, note that we regard the electric and magnetic fields as physically meaningful quantities even in those regions of space where there are no charged particles to interact with them. Although this might sound like a merely formal statement, it turns out to have profound consequences for our understanding of the physical dynamics of electric and magnetic fields.

Second, although we have provided a working definition of the electric and magnetic fields in terms of their influence on their surroundings, such a definition is void of physical meaning unless we also know how to predict the fields themselves from first principles.

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[1] In the study of electrodynamics, we opt to use the centimeter-gram-second (CGS) system of units rather than the International System of Units (SI) to simplify the form of the equations. The speed of light does not enter into the SI version of Eq. 1.1.

Formally, all physical properties of the electromagnetic field are embedded in a set of four relations known collectively as *Maxwell's Equations* after the Scottish scientist James Clerk Maxwell who (although he did not discover them) formulated them together into a coherent theory of electromagnetism. Together with the *Lorentz Force Law* of Eq. (1.1) and Newton's equations for material dynamics, Maxwell's Equations provide a complete description of the dynamics of both the electromagnetic field and the material systems with which it interacts. Unfortunately, the physical intuition embedded in these equations is often rather obscure to those encountering them for the first time. The next section offers a glimpse at this physical content, in preparation for the more technical discussion in the next chapter.

A Field by Any Other Name

One of the reasons electrodynamics can be confusing is that there are at least three distinct physical quantities that are sometimes referred to as the "electric field", and another three for the magnetic field. The quantities $e(x)$ and $b(x)$ defined by Eq. (1.1) are what are more precisely termed the *microscopic electric field* and *microscopic magnetic field*. Fundamentally, these fields are the basic quantities from which the other "fields" are derived. In the next chapter, we will introduce the *macroscopic fields* $E(x)$ and $B(x)$ which are obtained from the microscopic fields by coarse-graining over a small region of space. Finally, the derived fields $D(x)$ and $H(x)$ combine the macroscopic fields with the polarization of the surrounding material. All six of these quantities play important roles in electrodynamics, but they should not be confused with each other. In this text, we will primarily be concerned with the macroscopic fields, although in the first two chapters we will deal at some length with microscopic fields to see how they give rise to macroscopic electrodynamics.

1.2.2 The field as a flow map

So far, we have spoken of the electromagnetic field as a vector-valued map of electrical and magnetic forces. To understand the equations defining the field, it is helpful to view it from the slightly different (although compatible) perspective of a flow map. For most people, flow maps are perhaps more familiar in the context of water or air currents. For example, flow maps for global water currents depict the flow of water in oceanic cycles such as the gulf stream that warms eastern North America and western Europe. Mathematically speaking, the quantity represented in such maps – the magnitude and direction of water flow as a function of location – is a vector field, just like the electric and magnetic fields.

Borrowing intuitively from these more concrete examples, it turns out to be extremely useful to envision the electric and magnetic fields as similarly describing the flow of some (fictitious) electric or magnetic fluid through space. At each location in space, the field is then pictured as representing the magnitude and direction of flow of these imaginary fluids. It must be emphasized that such a picture should not be interpreted literally! Like all useful models, it is simply an analogy between one abstract quantity (the electric or magnetic

fields) and another, more familiar, one (the velocity field of a flowing current).

In this picture, the first two of Maxwell's equations embody rather intuitive concepts: electric charges act as either "sources" (positive charges) or "sinks" (negative charges) for the (fictitious!) electrical fluid. The magnetic fluid, in contrast, has no sources or sinks. More formally:

1. **Gauss's Law** says that the total flow rate of electrical fluid *out of* any closed surface is proportional to the total charge *enclosed by* the surface.

2. **Gauss's Law for Magnetism** says that the total flow rate of magnetic fluid out of any closed surface is zero.

The mathematical statement of Gauss's law is that

$$\nabla \cdot e = 4\pi\varrho(x, t) \tag{1.2}$$

where $\nabla \cdot e$ is the *divergence*

$$\nabla \cdot e = \frac{\partial e_x}{\partial x} + \frac{\partial e_y}{\partial y} + \frac{\partial e_z}{\partial z} \tag{1.3}$$

and where $\varrho(x, t)$ is the *charge density* function, defined by the property that the integral

$$\int_V dx \, \varrho(x, t) \tag{1.4}$$

gives the total charge contained in the volume V at time t. Without prior knowledge of multivariate calculus, it is by no means obvious that Eq. (1.2) is equivalent to a statement about flow rate through a surface. This connection is explained more precisely in the framed box below.

While Gauss's law says that charges act as sources and sinks for the electric field, Gauss's law for magnetism says that there *are no* sources or sinks for the magnetic field. Mathematically, this means that

$$\nabla \cdot b = 0. \tag{1.5}$$

At first, this non-existence of a sources might appear puzzling. If there are no magnetic "charges", then what *does* produce the magnetic field? As we will see next, the answer to this question lies embedded in the remaining two equations of Maxwell's theory.

Gauss's Theorem and the Differential form of Maxwell's Equations

To see the connection between the divergence operator $\nabla\cdot$ and flux through a surface, consider a simple quasi-two-dimensional example. Imagine an *incompressible* fluid flowing through a thin rectangular slab, as illustrated in Figure 1.1. For simplicity, we'll assume that the fluid flows only in the xy plane, so that we can ignore any flow in the z direction. In the two-dimensional projection on the bottom left, curved lines represent the pathways that would be followed by a small particle carried by the fluid. The density of these lines indicates the total velocity of the fluid in each region (more
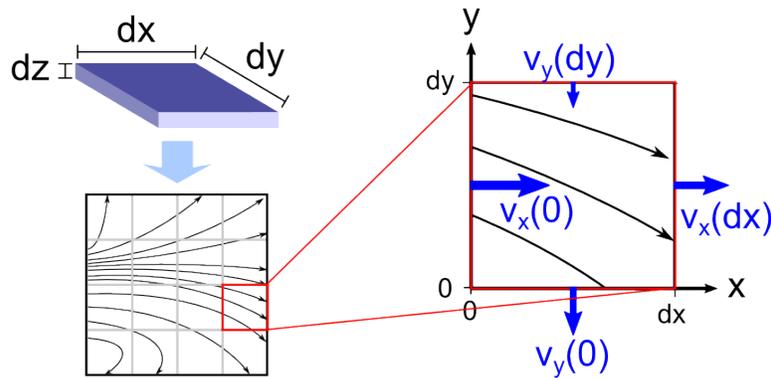
Figure 1.1: Flow rate of a fluid through a small region in two dimensions.

lines means a higher flow rate). Note that, because the fluid is assumed incompressible (a very accurate approximation for most real liquids), the density is constant throughout the fluid – only the fluid *velocity* varies with position. We now wish to ask: If we know the velocity field $v(x)$ of the fluid, how can we calculate the *total rate* at which fluid enters or exits the enclosed region?

The question is difficult to answer directly for the large region on the left since the flow rate varies considerably along the perimeter. However, for a sufficiently small rectangle (as shown at larger scale on the right-hand side), the flow rate can be assumed essentially constant along each of the four sides, so that the flow rate is characterized completely by the four velocity components $v_x(0)$, $v_x(dx)$, $v_y(0)$, and $v_y(dy)$, as labeled in the figure. For example, the flow rate of fluid *into* the region through the left-hand wall is simply $v_x(0)dydz$, while the flow rate *out* of the right-hand wall is $v_x(dx)dydz$. (Note that the total flow rate is proportional to $dydz$, the surface area of the wall.) Since the two flows have opposite signs, the total flow rate *out of* the region through the vertical walls is then

$$v_{\text{out}}^{(\text{vert})} = (v_x(dx) - v_x(0)) \, dydz. \tag{1.6}$$

The same analysis indicates that the total flow rate of fluid out of the horizontal walls is just

$$v_{\text{out}}^{(\text{horiz})} = \left(v_y(dy) - v_y(0) \right) dxdz. \tag{1.7}$$

Since we assumed the fluid to be flowing only in the xy plane, we can ignore fluid flow through the two surfaces perpendicular to the z axis, i.e., the top and bottom of the 3D

rectangle in the fiture.) The total flow rate of fluid *out* of the rectangle is thus

$$v_{\text{out}} = v_{\text{out}}^{(\text{vert})} + v_{\text{out}}^{(\text{horiz})} = \left(v_y(dy) - v_y(0)\right) dxdz + \left(v_x(dx) - v_x(0)\right) dydz. \tag{1.8}$$

Now, since the total volume of our rectangle is $dxdydz$, we can define a *outward flow rate per unit volume* as $\frac{v_{\text{out}}}{dx\,dy\,dz}$ which, as $dx, dy, dz \to 0$ converges to the limiting value

$$\lim_{dx,dy,dz \to 0} \frac{v_{\text{out}}}{dx\,dy\,dz} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y}. \tag{1.9}$$

An analogous calculation shows that if we had allowed the fluid to flow also along the z axis we would have obtained an additional term $\frac{\partial v_z}{\partial z}$, so that the general expression for the flow rate per unit volume of a 3D rectangle is exactly the divergence $\nabla \cdot \boldsymbol{v}$ [Eq. (1.3)] of the velocity flow field.

Finally, observe that the flow rate out of the large rectangle is simply the sum of the flow rates out of the small rectangles. Although we won't carry out the mathematical limit formally, the result is that in the limit that the number of rectangles goes to infinity, we obtain

$$v_{\text{out}}^{(\text{total})} = \lim_{N \to \infty} \sum_n v_{\text{out}}^{(n)} = \int dx \int dy\, \nabla \cdot \boldsymbol{v}(x, y). \tag{1.10}$$

When the total flow rate $v_{\text{out}}^{(\text{total})}$ is written as a surface integral over the velocity density, this last result is known in mathematics as *Gauss's Theorem*. It is this law that allows us to translate between the fluid flow density *at a single point* (characterized by the divergence) and the total flow rate *through a closed surface* as in our verbal statement of Gauss's laws for electricity and magnetism.

1.2.3 The field as a propagating wave

When the effects of electricity and magnetism were first discovered, they were viewed as separate quantities. Magnetic objects interacted with magnetic objects, and charged objects interacted with charged objects. Magnetic objects (it was believed) did *not* interact with charged objects or vice versa. The first two of Maxwell's equations (which we have just described) are consistent with this picture.

The essential content of Maxwell's last two equations, however, is that the electric and magnetic fields are in fact intricately connected. The reason this connection was at first missed is that it arises only for *dynamic* fields and vanishes under static conditions. In short, while it is true that a stationary magnet feels no force exerted on it by a stationary charged particle (and vice versa), the two objects *do* interact if they are in motion relative to each other.

Specifically, the final two of Maxwell's equations may be described as follows:

3. The **Maxwell-Faraday Equation** says that temporal changes in the magnetic field

produce "swirls" in the electric field.

4. **Ampere's Law** says that both flowing currents *and* temporal changes in the electric field produce "swirls" in the magnetic field

The word "swirl" here has a technical meaning, of course, but it is closely connected to the familiar notion of a swirl, eddy, or vortex in a flowing current. (See the box below.) Mathematically, the amount of "swirl" at a given location in a vector field (e, for example) is represented by the *curl* of the field

$$\nabla \times e = \begin{bmatrix} \frac{\partial e_z}{\partial y} - \frac{\partial e_y}{\partial z} \\ -\frac{\partial e_z}{\partial x} + \frac{\partial e_x}{\partial z} \\ \frac{\partial e_y}{\partial x} - \frac{\partial e_x}{\partial y} \end{bmatrix}. \tag{1.11}$$

If you point the thumb of your right hand in the direction of $\nabla \times e$, the swirl of the e field occurs in the same direction in which your fingers curl.

In terms of the curl, Maxwell's equations read

$$\nabla \times e + \frac{1}{c}\frac{\partial b}{\partial t} = 0 \tag{1.12}$$

and

$$\nabla \times b - \frac{1}{c}\frac{\partial e}{\partial t} = \frac{4\pi}{c} j(x, t), \tag{1.13}$$

where $j(x, t)$ is the *current density*, defined by the property that the total flow rate of electrical charge across any surface S is given by

$$\oint_S dS\, j \cdot \hat{n}, \tag{1.14}$$

where the integral extends over the entire surface S and where at each point on the surface S, the unit vector $\hat{n}$ extends in an outward direction, perpendicular to the surface.

Curls and Swirls

To see that the curl of Eq. (1.11) does indeed have something to do with "swirls" in flowing currents, consider again a simple two-dimensional example. Imagine a small stick floating on top of an eddy on the surface of a stream, as depicted on the left side of Figure 1.2. (The top panel depicts the stick oriented vertically along the y axis, while the bottom panel depicts the stick aligned horizontally with the x axis. We'll consider each case separately.) Now we ask: If the stick flows freely with the water, how fast does it rotate in the xy-plane?

Let's examine the vertically-oriented scenario first (top left). Beginning with a vertically-oriented stick at time $t = 0$, the top of the stick moves toward the right with velocity $\dot{x}_{top} = v_x(dy)$. At the same time, the bottom of the stick moves to the left by a displacement $\dot{x}_{bottom} = v_x(0)$. Now, at any time, the angle θ formed by the stick with
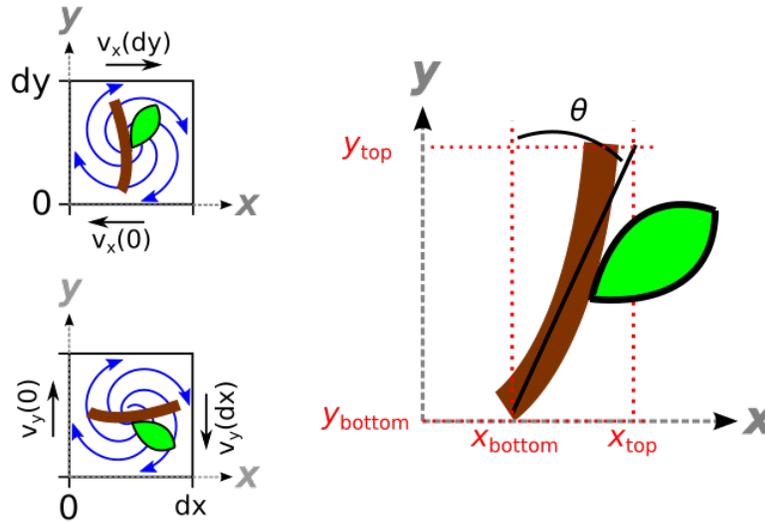
Figure 1.2: Schematic illustration of "swirls" in a velocity vector field.

the y axis is just

$$\theta(t) = \arcsin\left(\frac{x_{\text{top}}(t) - x_{\text{bottom}}(t)}{y_{\text{top}}(t) - y_{\text{bottom}}(t)}\right). \tag{1.15}$$

If the angle is very close to zero – as it should be for an initially-vertical stick and a short time interval dt – the series expansion $\sin(\theta) = \theta - \frac{\theta^3}{6} + ...$ implies that $\theta(t) \approx \frac{x_{\text{top}}(t) - x_{\text{bottom}}(t)}{y_{\text{top}}(t) - y_{\text{bottom}}(t)}$. Moreover, since the denominator changes only slightly, for small enough dt it can be assumed constant as $y_{\text{top}}(t) - y_{\text{bottom}}(t) = y_{\text{top}}(0) - y_{\text{bottom}}(0) = dy$. The rate at which $\theta(t)$ changes is thus simply

$$\dot{\theta} \approx \frac{\dot{x}_{\text{top}}(t) - \dot{x}_{\text{bottom}}(t)}{dy} = \frac{v_x(dy) - v_x(0)}{dy}, \tag{1.16}$$

which for a very short stick tends to the limit

$$\lim_{dx,dy\to 0} \dot{\theta}_{\text{vert}} = \frac{\partial v_x}{\partial y}. \tag{1.17}$$

Repeating this analysis for the horizontally-oriented stick, we find that in this case

$$\dot{\theta}_{\text{horiz}} \approx -\frac{\partial v_y}{\partial x}. \tag{1.18}$$

The negative sign appears because the right end of the stick now moves *down* along the y axis. On average, then, we find that an object dropped with a random orientation onto the eddy moves with an angular velocity

$$\omega_{\text{avg}} = \frac{\dot{\theta}_{\text{vert}} + \dot{\theta}_{\text{horiz}}}{2} = \frac{1}{2}\left(\frac{\partial v_x}{\partial y} - \frac{\partial v_y}{\partial v_x}\right). \tag{1.19}$$

Comparison with Eq. (1.11), shows that up to a factor of two and a sign change, this is just the z-component of the curl of the velocity vector field $v(x, y, z)$. Note that for an eddy "swirling" with the opposite sense (counterclockwise) ω_{avg} would have the same magnitude but an opposite sign. Thus, interpreted as a velocity flow map, the curl of a vector field indicates both the *magnitude* of "swirls" and their sense of rotation.

Fundamentally, these relations indicate a close coupling between the dynamics of the electric and magnetic fields: a changing E-field induces changes in the B-field and vice versa. In addition, Ampere's law tells us something quite important about the physical effects of moving charges, i.e. of electrical currents. We already know (from Gauss's law) that moving electrical charges produce changes in the electric field. Ampere's law tells us in addition that *moving electrical charges produce magnetic fields*. At a fundamental level, these two equations thus explain why magnetic fields exist even in the absence of "magnetic charges": the ultimate origin of the magnetic field is in electrical charges, just as for the electric field. The difference is that the magnetic field is produced by *moving* electrical charges (or temporal changes in the electric field), while the electrical field is produced by *static* charges[2] (or temporal changes in the magnetic field).

This dynamical coupling between the electric and magnetic fields has profound implications for the laws of physics. Because the two fields exist and interact even in regions of space where there are no electrical charges, *the coupled electric and magnetic fields can propagate through space even in the absence of any material medium*. Conceptually, this propagation can be visualized as follows: A changing electric field at one location in space (e.g. originating from the motion of charged particles) induces a magnetic field in the regions adjacent to it; since the electric field is changing in time, these induced magnetic fields also change in time. Now, these changing magnetic fields (a small distance away from the initial source) likewise produce changing electric fields in their vicinities, which in turn induces magnetic fields even farther from the original source.

Mathematically, this propagating field behaves like a propagating wave, much like a ripple on the surface of a pond – only without the pond! Physically, this propagating electromagnetic wave is recognized as *electromagnetic radiation*. Electromagnetic radiation of certain frequencies (i.e. certain length of "ripples") is detectable by the human eye and is recognized as *light*, although we will usually use the terms "electromagnetic radiation," "electromagnetic waves," and "light" interchangeably. The interaction of these propagating fields with material systems constitutes the whole subject of spectroscopy.

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[2]Of course, moving charges also produce electric fields, in addition to magnetic fields.

1.3   Light-Matter Interactions & Spectroscopy

So far, we've touched on three of the main principles that are at work in any spectroscopic experiment. In no particular order:

1. All matter is made of charged particles.

2. Electromagnetic waves, consisting of an oscillating electric and magnetic field, exist.

3. Electromagnetic waves exert an oscillatory force on the charged particles that make up matter in accordance with the Lorentz force law.

In fact, we're missing just a single detail to (very broadly) summarize most of spectroscopy

4. When a charged particle is accelerated (or decelerated) it radiates electromagnetic waves.

This last point is not obvious from simply looking at Maxwell's equations and the Lorentz force law, but it is not to hard to show that this is indeed the case. (In fact, we will see this explicitly in §2.3.4, but for now let's take it on faith.)

Essentially, spectroscopy consists of these four steps. There's some stuff (made of charged particles) that we're interested in learning about (maybe it's a molecule). We shine electromagnetic waves on the stuff that exert an oscillatory force on the charged particles in the stuff, causing the charged particles to accelerate. As the charged particles accelerate back and forth, they emit more electromagnetic waves that we then measure. Sometimes we can detect these waves directly (such as in fluorescence), and other times we can only detect these wave via *interference* with the waves we're shining in (such as in absorption).

What do these waves tell us about the stuff? Let's consider a molecule to be more specific. In addition to the force we're applying by shining light on the charges in the molecule, there are a plethora of electrostatic forces binding these charges together. This means that the charges can only oscillate *resonantly* at certain frequencies that are determined by the binding forces in the molecule. So by discovering which frequencies cause a large response, we learn about the molecular binding forces and thus the molecular structure. Other times, we'll be interested in learning about the dynamics of the charged particles, and this is where time-resolved spectroscopic techniques come in.

This raises the question of what waves we should be sending into our system in order to best study it. To this end, there are essentially two approaches. First, we may send in waves of a well defined frequency and scan this frequency until we see a large response. In this way, we can map out the resonances in the system over broad frequency ranges. On the other hand, we may try to "kick" the system as hard as we can with a short pulse of light and observe at which frequencies the resonances occur. These methods, termed "continuous wave" (CW) and "pulsed", respectively, fundamentally give the same information, but oftentimes one is preferable over the other due to practical considerations or ease of obtaining the desired

information. We will largely focus on pulsed experiments in what follows, but we'll have occasion to discuss CW techniques as well.

Before diving in to mathematically describing the phenomena discussed in this section, there's a fundamental aspect we need to address. The charged particles we have been discussing are, for our purposes, *point particles* – particles with no spatial extent, existing at a single point in space. While this description turns out to be physically correct[3] (at least as far as we can tell), it introduces some technical difficulties in the equations that we now address.

1.4 Inconvenient Infinities

As emphasized in the description of the Lorentz force law [Eq. (1.1)], our formulation of electrodynamics employs a number of simplifying assumptions. Although these simplifications are standard in most textbooks, they can themselves create substantial confusion since, if not introduced and interpreted consistently, they can actually render many fundamental equations mathematically undefined. This section examines these issues in more detail.

Fundamentally, these complications arise from an apparently simple physical question: What are the physical dimensions of a charged particle? In the early days of electrodynamics (before the introduction of quantum theory), charged particles were typically assumed to be concrete objects with finite spatial dimensions, e.g., spheres or ellipsoids of a (roughly) fixed size. Under this classical theory, our statement of the Lorentz force law [Eq. (1.1)] cannot be fundamentally correct since it samples the field at only a single point: a charged particle with a finite size ought instead to "feel" the electric and magnetic fields at *all* points within its volume. Although we could incorporate such finite-size effects into our equations by integrating over the charge volume, the additional complication is, for our purpsoses, entirely unnecessary. So long as the particle dimensions are very small and we only consider dynamics on length scales much larger than those dimensions, Eq. (1.1) will be an excellent approximation to (classical) reality. This first simplifying assumption will be maintained throughout this course, i.e., we will always neglect any finite spatial extent of fundamental particles.

In electrodynamics, this neglect of finite-size effects is usually summarized by saying that we deal only with *point particles*: objects that have a finite charge but no finite spatial extent. In many cases, the point-particle perspective drastically simplifies the mathematical complexity of electrodynamic expressions and allows for much simpler physical interpretation of their content. Unfortunately, if not introduced carefully, the point-particle approximation also introduces serious internal inconsistencies into the fundamental equations of electrodynamics. In short, although extremely useful, the point-particle approximation must be applied with care!

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[3]It is at least correct for electrons. Nuclei contain protons and neutrons, which in turn contain up quarks and down quarks. Even though the quarks in the nucleus are the only point particles, it'll be an excellent approximation to treat the nucleus itself as a point particle at all the energies we'll be considering.

To see how inconsistencies can arise (and how to avoid them) consider the charge and current densities $\rho(\boldsymbol{x}, t)$ and $\boldsymbol{j}(\boldsymbol{x}, t)$ introduced in the last section. In a strict point-particle theory, the charge and current densities take the form

$$\varrho(\boldsymbol{x}, t) \approx \sum_n q_n \delta\left(\boldsymbol{x} - \boldsymbol{r}_n\right) \tag{1.20}$$

and

$$\boldsymbol{j}(\boldsymbol{x}, t) \approx \sum_n q_n \boldsymbol{v}_n \delta\left(\boldsymbol{x} - \boldsymbol{r}_n\right) \tag{1.21}$$

where q_n, $\boldsymbol{r}_n$, and $\boldsymbol{v}_n$ are, respectively, the charge, position, and velocity of the nth particle and the use of the approximation sign "$\approx$" again serves to highlight that these equations are only valid when finite-size effects can be neglected. The function $\delta(\boldsymbol{x})$ in Eqs. (1.20) and (1.21) is the *Dirac delta function* defined by the property[4] that, for any three-dimensional volume V,

$$\int_V d\boldsymbol{x}\, \delta(\boldsymbol{x} - \boldsymbol{x}_o) f(\boldsymbol{x}) = \begin{cases} f(\boldsymbol{x}_o), & \boldsymbol{x}_o \in V \\ 0, & \boldsymbol{x}_o \notin V. \end{cases} \tag{1.22}$$

Thanks to this ability to eliminate integrals, working with delta functions considerably simplifies many otherwise-difficult mathematical expressions. In electrodynamics, its appearance in the charge and current densities reflects the fact that particles with no finite spatial extent contribute either all or none of their charge to integrated quantities (such as the total charge of Eq. (1.4) or the charge flow rate of Eq. (1.14)) depending on whether or not they are contained inside the integration volume.

Unfortunately, it is easily verified that no real mathematical function satisfies the property (1.22) used to "define" the Dirac delta function. The proper resolution to this inconsistency is *either* to abandon the point-particle picture altogether *or* to invoke more powerful mathematical tools such as distribution and measure theory. Instead, physical scientists tend to "embrace the paradox," opting for the intuitive appeal of Eq. (1.22), despite its internal inconsistency. Perhaps surprisingly, this approach works just fine for *most* electrodynamic calculations. For example, Gauss's law [Eq. (1.2)] and Ampere's law [Eq. (1.13)] remain mathematically rigorous (in a distribution-theory sense) even when the delta-function forms for $\rho(\boldsymbol{x}, t)$ and $\boldsymbol{j}(\boldsymbol{x}, t)$ are introduced on their right-hand sides. The use of delta functions in Maxwell's equations – and all equations derived solely from them – is thus internally consistent.

However, the Lorentz force law – and certain expressions derived from it – become ill-defined in the presence of delta-function densities. In fact, we will see in Section 2.3.3, that the magnitude of the electric field always diverges as $1/r^2$ as the distance r to the nearest point particle decreases (see Figure 1.3. Such divergences cause the Lorentz force

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[4]Strictly speaking, the integral is undefined for points lying on the boundary of the volume. E.g., if V is a closed sphere with $\boldsymbol{x}_o$ lying on its surface, the integral has no well-defined value.
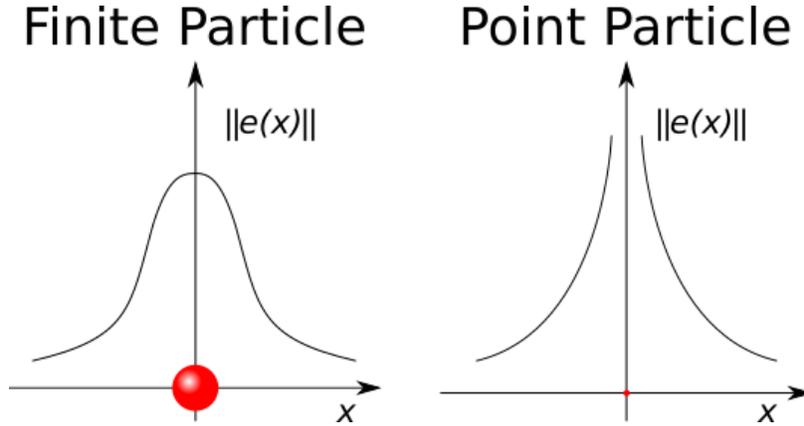
Figure 1.3: Schematic illustration of the electric field in the vicinity of a finite-sized particle (left) and point particle (right). Near a finite-size particle, the field approaches a stable maximum, while it diverges in the vicinity of the point particle.

law [Eq. (1.1)] to become mathematically ill-defined since the electric field at the particle position is infinite. A similar divergence is encountered in calculations involving the total energy content of the electromagnetic field [Eq. (2.50)] due to the infinite *self-energy* of each point particle repelling itself.

A self-consistent point-particle theory can be developed by eliminating such infinities "by hand," e.g., by replacing the electric field in Eq. (1.1) with the "effective field"

$$e^{(\text{eff})} = \lim_{r' \to r} \left(e(r') - q\frac{r}{|r' - r|^2} \right) \tag{1.23}$$

to obtain

$$F_{\text{EM}} = qe^{(\text{eff})} + q\frac{v}{c} \times b(r), \tag{1.24}$$

which eliminates self-interaction terms from the force. This approach is exactly what is necessary, for example, to produce the Coulomb force [Eq. (2.83)] that governs particle-particle interactions in the near-field limit.

In this course, we will regard Eq. (1.24) as the fundamental equation that, together with Maxwell's equations, defines *point-particle* electrodynamics. On the other hand, our earlier statement, Eq. (1.1), is an approximate expression that defines the *total* force felt by a *finite* particle which is small enough that spatial variations in the field can be neglected. Thus both statements [Eqs. (1.1) and (1.24)] are to be understood as approximations to a more rigorous classical electrodynamic theory that involves finite, rigid, spherical, charged particles.[5]

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[5]In a rigorous quantum field theoretic treatment of fundamental particles these infinites cannot be swept under the rug since fundamental particles are indeed point particles (as far as we can tell). This has led scientists to come up with clever (albeit confusing) ways to deal with the equations that have produced the most accurate physical theories to date.

With this warning stated, it should be emphasized that the distinction between Eqs. (1.1) and (1.24) will usually be irrelevant to our work. In fact, only in Section 2.2 does the distinction play any fundamental role; and, even in this case, the only results that we use regularly (the definitions for the *vacuum* electromagnetic energy density and Poynting vector) are independent of the representation.

Chapter 2

Electrodynamics

The last chapter introduced four fundamental equations for electrodynamics:

$$\nabla \cdot \boldsymbol{e} = 4\pi\varrho(\boldsymbol{x}, t) \tag{2.1a}$$

$$\nabla \cdot \boldsymbol{b} = 0 \tag{2.1b}$$

$$\nabla \times \boldsymbol{e} + \frac{1}{c}\frac{\partial \boldsymbol{b}}{\partial t} = 0 \tag{2.1c}$$

$$\nabla \times \boldsymbol{b} - \frac{1}{c}\frac{\partial \boldsymbol{e}}{\partial t} = \frac{4\pi}{c}\boldsymbol{j}(\boldsymbol{x}, t) \tag{2.1d}$$

which, together with the Lorentz force law [Eq. (1.1)] and Newton's equations provide a complete description of the dynamics of charged particles. In practice, of course, actually solving these equations is quite difficult. In this section, we begin with a discussion of electromagnetic fields in vacuum, before turning to the much more complicated topic of electrodynamics in material systems.

2.1 The Electromagnetic Field in Vacuum

2.1.1 Decoupling the Electric and Magnetic Fields

In this section, we take the results of the previous section and derive the properties of the electric and magnetic induction fields in vacuum (that is, in the absense of any matter), focusing on electromagnetic waves which we commonly refer to as light. In the presense of matter, the vacuum description breaks down, but it is a useful and accurate approximation to electromagnetic fields propagating in rare media, such as air. Furthermore, it will set the stage for the following chapter when we consider the interaction of electromagnetic waves, that is, light, with macroscopic systems.

In vacuum, Maxwell's Equations read

$$\nabla \cdot e(x, t) \;=\; 0, \tag{2.2a}$$

$$\nabla \cdot b(x, t) \;=\; 0, \tag{2.2b}$$

$$\nabla \times e(x, t) + \frac{1}{c}\frac{\partial b(x, t)}{\partial t} \;=\; 0, \tag{2.2c}$$

$$\nabla \times b(x, t) - \frac{1}{c}\frac{\partial e(x, t)}{\partial t} \;=\; 0. \tag{2.2d}$$

At first, the coupling between the electric and magnetic fields makes these equations look rather intimidating. A brief rearrangement, however, brings them into a much simpler form. Taking the curl of Eq. 2.2c and using Eq. 2.2d to eliminate the curl of B gives

$$\nabla \times (\nabla \times e(x, t)) + \frac{1}{c^2}\frac{\partial^2 e(x, t)}{\partial t^2} \;=\; 0. \tag{2.3}$$

We thus obtain a linear differential equation for the electric field alone, decoupled from the magnetic field. In light of the vector identity

$$\nabla \times (\nabla \times \mathbf{v}) = -\nabla^2 \mathbf{v} + \nabla(\nabla \cdot \mathbf{v}) \tag{2.4}$$

(valid for any vector field $\mathbf{v}$) and Eq. (2.2a) for the electric field in vacuum, this becomes

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 \right) e(x, t) = 0. \tag{2.5}$$

An identical equation holds for the microscopic magnetic field.

2.1.2 Propagating Waves

Equation 2.5 is really three independent differential equations, one for each component of the electric field. Each component equation has the form of the *homogenous wave equation*

$$\frac{1}{c^2}\frac{\partial^2 f}{\partial t^2} - \nabla^2 f = 0. \tag{2.6}$$

Remarkably, this equation is satisfied by *any* function of the form $f(\hat{s} \cdot x \pm ct)$, where $\hat{s}$ is any unit vector. Indeed, a brief calculation reveals that

$$-\nabla^2 f(\hat{s} \cdot x \pm ct) = -\hat{s} \cdot \hat{s} f''(\hat{s} \cdot x \pm ct) = -f''(\hat{s} \cdot x \pm ct) \tag{2.7}$$

and similarly that

$$\partial_t^2 f(\hat{s} \cdot x \pm ct) = c^2 f''(\hat{s} \cdot x \pm ct) \tag{2.8}$$

Substituting these results into Eq. 2.6, shows that the equation is indeed satisfied.

Functions of the form $f(\hat{s} \cdot x \pm ct)$ propagate in time without changing shape. That is, at some instant in time, say $t = 0$, f will be a certain function of the spatial variable $\hat{s} \cdot x$. At some time τ later, f will have the same form as a function of x, but will be shifted in the $\hat{s}$ direction by an amount $\pm c\tau$. Choosing the minus sign results in propagation in the $+\hat{s}$ direction while the plus sign corresponds to propagation in the $-\hat{s}$ direction.

2.1.3 Fourier Transforms

The results from the previous section indicate that Eq. (2.5) may be solved by setting each component of the electric field to a function $e_i(\hat{s}_i \cdot \boldsymbol{x} \pm ct)$. This does not, however, tell us immediately whether there are other possible solutions. To answer this more general question, we make use of an mathematical tool of great value in spectroscopy: the Fourier transform.

The *Fourier transform* of a single-variable function $g(t)$ is defined as

$$\tilde{g}(\omega) = \int_{-\infty}^{\infty} dt \, \mathrm{e}^{\mathrm{i}\omega t} g(t). \tag{2.9}$$

The complex function $\tilde{g}(\omega)$ has a simple interpretation: the amplitude at a given ω is how much of a particular frequency is present in the original function $g(t)$, and the phase at a given ω is the phase of that frequency component. In this way, a complicated function $g(t)$ can be broken into its basic frequency components in the same way that a musical chord can be broken down into its constituent notes. The functions $\tilde{g}(\omega)$ and $g(t)$ are referred to as a Fourier transform pair. An important property of the Fourier transform is that it is linear, as is evident from its definition.

The only function that carries within it a single frequency $g(t)$ is the complex exponential $\mathrm{e}^{-\mathrm{i}\omega_0 t}$, whose transform is a delta function at ω_0. The cosine function $\cos(\omega_0 t)$ which is just the sum of $\mathrm{e}^{\mathrm{i}\omega_0 t}/2$ and $\mathrm{e}^{-\mathrm{i}\omega_0 t}/2$ has a Fourier transform with two frequency components: delta functions at $\pm\omega$, as we expect from the linearity of the transform. Table 2.1 lists a few of the most useful transforms and properties.

The Fourier transform of a function that's narrow in the time domain is broad in the frequency domain and vice versa. This is because in order to have a narrow time-domain function, it is necessary for many frequencies to contribute to coherently add to give a signal localized in time. This has profound consequences in spectroscopy. A molecule with a sharp absorption resonance (narrow in the frequency domain) posses a transition dipole that oscillates for a long time (broad in the time domain). This allows, under certain circumstances, for the lifetime of transition to be determined from the width of the spectrum.

$g(t)$	$\tilde{g}(\omega)$
$\mathrm{e}^{-\mathrm{i}\omega_0 t}$	$2\pi\delta(\omega - \omega_0)$
$\cos(\omega_0 t + \phi)$	$\pi\left(\delta(\omega + \omega_0)\mathrm{e}^{\mathrm{i}\phi} + \delta(\omega - \omega_0)\mathrm{e}^{-\mathrm{i}\phi}\right)$
$\mathrm{e}^{-at}\cos(\omega_0 t + \phi)u(t)$	$\frac{(\mathrm{i}\omega - a)\cos\phi + \omega_0 \sin\phi}{(\mathrm{i}\omega - a)^2 + \omega_0^2}$
$\mathrm{e}^{-\frac{t^2}{2\sigma^2}}$	$\sqrt{2\pi}\sigma\mathrm{e}^{-\frac{1}{2}\sigma^2\omega^2}$
$g(t - t_0)$	$\tilde{g}(\omega)\mathrm{e}^{\mathrm{i}\omega t_0}$
$g(t)\mathrm{e}^{\mathrm{i}\omega_0 t}$	$\tilde{g}(\omega + \omega_0)$

Table 2.1: Fourier transform of common functions. $u(t)$ is the unit step function

Importantly, the Fourier transform is invertible. We may recover the original function

$g(t)$ through the *inverse Fourier transform*

$$g(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, e^{-i\omega t} \tilde{g}(\omega). \tag{2.10}$$

Where we put the $1/\sqrt{2\pi}$ prefactor is a matter of convention, and we could have just as easily put it on the forward transform or split it between the two.

Note that if $g(t)$ is real, it is easy to show that

$$\tilde{g}(\omega)^* = \tilde{g}(-\omega), \tag{2.11}$$

where the "$*$" indicates the complex conjugate. It's a little more challenging to show that if $g(t)$ is a real, symmetric function such that $g(t) = g(-t)$, then its Fourier transform is real and given by

$$\tilde{g}(\omega) = 2 \int_0^{\infty} dt \, \cos(\omega t) g(t). \tag{2.12}$$

The Fourier transform is useful in solving differential equations because it converts derivatives into simple products. Consider what happens when we take the Fourier transform of a time-derivative:

$$\widetilde{\frac{dg}{dt}} = \int_{-\infty}^{\infty} dt \, e^{i\omega t} \frac{dg}{dt}. \tag{2.13}$$

Integration by parts gives

$$\widetilde{\frac{dg}{dt}} = e^{i\omega t} g(t) \Big|_{-\infty}^{\infty} - i\omega \int_{-\infty}^{\infty} dt \, e^{i\omega t} g(t) = -i\omega \tilde{g}(\omega), \tag{2.14}$$

where we have assumed that $g(t)$ decays to zero as $|t| \to \infty$. (In fact the Fourier transform itself is undefined otherwise!)

For a field such as $e(\boldsymbol{x}, t)$, which is a function of both space and time, we similarly define a multi-dimensional Fourier transform

$$\tilde{e}(\boldsymbol{k}, \omega) = \int_{-\infty}^{\infty} d\boldsymbol{x} \int_{-\infty}^{\infty} dt \, e^{i(\omega t - \boldsymbol{k} \cdot \boldsymbol{x})} e(\boldsymbol{x}, t), \tag{2.15}$$

which satisfies the inverse transform relation

$$e(\boldsymbol{x}, t) = \frac{1}{(2\pi)^4} \int_{-\infty}^{\infty} d\boldsymbol{k} \int_{-\infty}^{\infty} d\omega \, e^{-i(\omega t - \boldsymbol{k} \cdot \boldsymbol{x})} \tilde{e}(\boldsymbol{k}, \omega). \tag{2.16}$$

Note that we have chosen a different sign between the ωt and $\boldsymbol{k} \cdot \boldsymbol{x}$ terms. This is purely a convention, which we choose to agree with the solutions to the wave equation that propagate in the $+\hat{\boldsymbol{k}}$ direction. In this multi-variable form, Eq. (2.14) becomes

$$\widetilde{\frac{\partial e(\boldsymbol{x}, t)}{\partial x_i}} = i k_i \tilde{e}(\boldsymbol{k}, \omega) \tag{2.17}$$

for each $i = 1, 2, 3$, and

$$\widetilde{\frac{\partial e(x, t)}{\partial t}} = -i\omega \tilde{e}(k, \omega). \tag{2.18}$$

Note that since $e(x, t)$ is real-valued, the Fourier transform $\tilde{e}(x, \omega)$ must satisfy the symmetry relation

$$\tilde{e}(-k, -\omega) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dt \, e^{-i(\omega t - k \cdot x)} e(x, t) = \tilde{e}^*(k, \omega), \tag{2.19}$$

2.1.4   The General Solution to Maxwell's Equations in Vacuum

What do these transforms have to do with solutions to the wave equation? Applying the derivative rule twice, we find that Fourier transformation of the wave equation [Eq. (2.5)] gives

$$\left(-\frac{\omega^2}{c^2} + |k|^2 \right) \tilde{e}(k, \omega) = 0. \tag{2.20}$$

This equation is satisfied *if and only if* the Fourier-transformed field $\tilde{e}(k, \omega)$ is non-zero only for points satisfying the relation

$$|k| = \frac{\omega}{c}. \tag{2.21}$$

The relationship between the magnitude of k and ω in the wave equation is known as a *dispersion relation*; in vacuum, it is a linear relation. Inverting the Fourier transform, this implies that the most general form possible for an electromagnetic field in a vacuum is given by Eq. (2.16), where $\tilde{e}(k, \omega)$ is any function that satisfies Eq. (2.21).

   Finally, note that although the magnetic field follows a wave equation of the same form, the electric and magnetic fields are *not* independent. In fact, Fourier-transforming Eq. (2.2c) gives

$$k \times \tilde{e}(k, \omega) = \frac{\omega}{c} \tilde{b}(k, \omega) \tag{2.22}$$

or, in light of Eq. (2.21),

$$\tilde{b}(k, \omega) = \frac{k}{|k|} \times \tilde{e}(k, \omega). \tag{2.23}$$

Equivalently, Gauss's law for magnetism gives

$$\tilde{e}(k, \omega) = -\frac{k}{|k|} \times \tilde{b}(k, \omega). \tag{2.24}$$

Thus once the electric field is specified, the magnetic field is completely determined.

2.1.5 Plane Waves

Although Eq. (2.16) gives a general form for electromagnetic fields in vacuum, the fields encountered in spectroscopy are often highly idealized. In particular, instead of including a continuous integral over possible $\boldsymbol{k}$ vectors, we will typically assume that the field can be well approximated by a finite sum:

$$e(\boldsymbol{x}, t) = \frac{1}{2\pi} \sum_i \int_0^\infty d\omega\, \tilde{\boldsymbol{A}}^{(i)}(\omega)\mathrm{e}^{-\mathrm{i}\frac{\omega}{c}\left(ct - \hat{\boldsymbol{s}}^{(i)}\cdot\boldsymbol{x}\right)} + \text{c. c.} \tag{2.25}$$

In comparison to Eq. (2.16), we have simply replaced the integral over $\boldsymbol{k}$ with a discrete sum over unit vectors $\hat{\boldsymbol{s}}^{(i)}$, using the dispersion relation [Eq. (2.21)] to fix the length of the wavevector. Note that each term has a different amplitude and phase, $\tilde{\boldsymbol{A}}^{(i)}$. Eq. (2.25) also incorporates a nonessential change in notation: the lower integration limit of ω has been changed from $-\infty$ to 0, while "+c. c." (for "plus complex conjugate") has been added at the end of the expression. This is purely a notational change since the symmetry relation [Eq. (2.19)] (and hence $\tilde{\boldsymbol{A}}^{(i)}(\omega) = \left[\tilde{\boldsymbol{A}}^{(i)}(-\omega)\right]^*$) implies that the integral from $-\infty$ to 0 is exactly captured by the +c. c. term.

Each term in the sum [Eq. (2.25)] can be thought of as representing a different *plane wave* in the laboratory, i.e., a component of the electromagnetic field that has a well-defined propagation axis $\hat{\boldsymbol{s}}^{(i)}$. It's a fundamental feature of Maxwell's equations that any component of the electromagnetic field with a well-defined propagation axis has infinite spatial extent in the plane perpendicular to the propagation axis, hence the name. Of course, this is unphysical; any real field will have a finite spatial extent even if it has a relatively well-defined propagation axis, as most lasers do. That is, a real field will have an intensity profile that decays in the plane perpendicular to its principal propagation direction (typically called a "beam"); this requires a continuous distribution of $\boldsymbol{k}$ vectors that give rise to effects that alter the intensity profile as the field propagates. For most purposes, however, we will not need to consider these effects explicitly, and plane waves capture most of what we care about. Since we will deal with plane waves quite extensively, it is worth investigating their properties in some detail.

Consider an idealized plane wave of the form

$$e(\boldsymbol{x}, t) = \frac{1}{2\pi} \int_0^\infty d\omega\, \tilde{\boldsymbol{A}}(\omega)\mathrm{e}^{-\mathrm{i}\frac{\omega}{c}(ct - \hat{\boldsymbol{s}}\cdot\boldsymbol{x})} + \text{c. c.} \tag{2.26}$$

The complex, vector-valued function $\tilde{\boldsymbol{A}}(\omega)$ in Eq. (2.26) specifies both the *polarization* of the wave (the axis along which the field is directed at a given point in time and space) and its *spectrum*, i.e., the amplitudes and phases of all its frequency components in Fourier space. Note that we have not restricted a plane wave to be of a single frequency, and by our definition a plane wave can support any polarization, amplitude, or phase.[1] In fact,

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[1] In the literature, the term plane wave is often (and incorrectly) used to mean time-harmonic (i.e. single frequency) wave. The "plane" of course refers to the spatial extent of the wave and not the spectrum.

in Fourier space, the plane wave of Eq. (2.26) is proportional simply to a delta function around $\boldsymbol{k} = \frac{\omega}{c}\hat{s}$

$$\tilde{e}(\boldsymbol{k}, \omega) = 8\pi^3 \tilde{\boldsymbol{A}}(\omega)\delta\left(\boldsymbol{k} - \frac{\omega}{c}\hat{s}\right) \tag{2.27}$$

as may be seen directly by applying the definition [Eq. (2.15)] and noting that[2]

$$\int dt\, e^{i\omega t}e^{-i\omega' t} = 2\pi\delta(\omega - \omega'). \tag{2.28}$$

From Eq. (2.23), the magnetic field is similarly found to be

$$\tilde{\boldsymbol{b}}(\boldsymbol{k}, \omega) = 8\pi^3 \hat{s} \times \tilde{\boldsymbol{A}}(\omega)\delta\left(\boldsymbol{k} - \frac{\omega}{c}\hat{s}\right) \tag{2.29}$$

or in the time domain simply

$$\boldsymbol{b}(\boldsymbol{x}, t) = \hat{s} \times \boldsymbol{e}(\boldsymbol{x}, t). \tag{2.30}$$

Thus the electric and magnetic fields are perpendicular at all times. Moreover, Eq. (2.24) implies that

$$\boldsymbol{e}(\boldsymbol{x}, t) = -\hat{s} \times \boldsymbol{b}(\boldsymbol{x}, t), \tag{2.31}$$

implying that the electric field is also perpendicular to $\hat{s}$. We therefore find that the three vectors $\hat{s}$, $\boldsymbol{e}(\boldsymbol{x}, t)$, and $\boldsymbol{b}(\boldsymbol{x}, t)$ are mutually orthogonal at every point in time and space, with the axes $\{\hat{s}, \hat{e}, \hat{b}\}$ forming a right-handed coordinate system.

A plane wave is said to be *polarized* if $\tilde{\boldsymbol{A}}(\omega)$ can be factored as the product of a scalar spectral function $\tilde{A}(\omega)$ and a time-independent (possibly complex) *polarization vector* $\hat{\epsilon}$ of unit length:[3]

$$\boldsymbol{e}(\boldsymbol{x}, t) = \frac{\hat{\epsilon}}{2\pi}\int_0^\infty d\omega\, \tilde{A}(\omega)e^{-i\frac{\omega}{c}(ct - \hat{s}\cdot\boldsymbol{x})} + \text{c. c.} \tag{2.32}$$

Since the field is orthogonal to $\hat{s}$, the polarization vector $\hat{\epsilon}$ may always be written as a sum

$$\hat{\epsilon} = a\hat{\epsilon}_1 + e^{i\phi}b\hat{\epsilon}_2 \tag{2.33}$$

where $a^2 + b^2 = 1$ and where $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ are real, orthogonal, unit vectors that are each perpendicular to $\hat{s}$.

The field is said to be *linearly polarized* if $\phi = 0$, i.e., if the field dynamics along the two axes $\hat{\epsilon}_1$ and $\hat{\epsilon}_1$ are in phase with each other. In this case, the electric field always points along the axis $\hat{\epsilon}$, while the magnetic field points along the perpendicular axis $\hat{s} \times \hat{\epsilon}$.

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[2]Apart from the usual caveats regarding the use of delta functions, this follows directly from the definition [Eq. (2.9)] of the Fourier transform applied to the delta function and the relationship [Eq. (2.10)]

[3]The "length" of a complex vector is defined as $\|\boldsymbol{v}\| = \sqrt{\boldsymbol{v}^* \cdot \boldsymbol{v}}$. The conjugation is necessary to ensure that the resulting length is always a real number.

If ϕ is nonzero, the field components along the two polarization axes are out of phase with each other, and the polarization dynamics are more complicated. Such a field is said to be *eliptically polarized*. As a simple example, consider a *monochromatic* field where

$$\tilde{A}(\omega) = \frac{\delta(\omega - \omega_o)}{2\pi} \tag{2.34}$$

so that

$$e(x, t) = a\hat{\epsilon}_1 \cos\left(\frac{\omega_o}{c}\left(ct - \hat{s} \cdot x\right)\right) + b\hat{\epsilon}_2 \cos\left(\frac{\omega_o}{c}\left(ct - \hat{s} \cdot x\right) + \phi\right). \tag{2.35}$$

For fixed x, the field polarization traces out an ellipse with a frequency ω_o. When $a = b$, this ellipse becomes a circle, and the field is said to be *circularly polarized*.

For general (not monochromatic) elliptically-polarized waves, the shapes traced out by the electric field are more complex. At a fixed point in space, the total field traces out a complicated pattern in time due to the fact that each frequency component completes a single "trace" with a different frequency.

2.2   Field-Particle Interactions: Force, Work, and Energy

Implicit in Maxwell's theory is the recognition that the electromagnetic field can transport energy. Indeed, the Lorentz force law [Eq. (1.1)] indicates that the field does work on charged particles, while the propagating waves we observed in the last section show that a field generated in one region of space can propagate to others, carrying with it the potential to do such work. In this section, we will examine this concept in more detail. Specifically, we will develop a measure for the *quantity* of energy carried by a given electromagnetic wave.

2.2.1   Electromagnetic Work

In classical mechanics, the work performed on a particle is calculated as an integral of force exerted over distance:

$$W = \int_{r(t_1)}^{r(t_2)} dr \cdot F(r). \tag{2.36}$$

Here $r(t_1)$ and $r(t_2)$ are the initial and final positions of the particle of interest, and $F(r)$ is the force exerted on the particle at each point along its path. Since $dr = v(t)dt$, this can be rewritten as

$$W = \int_{t_1}^{t_2} dt\, v \cdot F(r(t)). \tag{2.37}$$

To calculate the electromagnetic work performed on a particle, we need only evaluate this last expression with the total force $F(r(t))$ replaced by the electromagnetic component

governed by the Lorentz force law. Here, however, we are for the first time forced to choose between the two versions of this law stated in Chapter 1, i.e., Eqs. (1.1) and (1.24). For true point particles, Eq. (1.24) is to be regarded as the correct expression, while Eq. (1.1) describes the total force exerted on a rigid, *finite* particle with very small spatial dimensions. As it turns out, this section is one of the few points in our discussion where the distinction really matters: as we will see shortly, several of the identities we will derive in this section are ill-defined in the point-particle picture.

Proceeding with the (approximate) finite-particle Lorentz force law [Eq. (1.1)], the electromagnetic component of the work done on an assembly of charged particles becomes

$$W_{\text{el}} = \sum_n q_n \int_{t_1}^{t_2} dt\, \boldsymbol{v}_n(t) \cdot \boldsymbol{e}(\boldsymbol{r}_n, t) \tag{2.38}$$

$$= \int_{t_1}^{t_2} dt \int_V d\boldsymbol{x} \left(\sum_n q_n \boldsymbol{v}_n(t) \delta\left(\boldsymbol{x} - \boldsymbol{r}_n\right) \right) \cdot \boldsymbol{e}(\boldsymbol{x}, t), \tag{2.39}$$

where in the second line we have used Eq. (1.22) to rewrite the expression as an integral over some volume V that contains the material system (and no other particles). Since the magnetic force is always perpendicular to the velocity of the particle, it can do no work.

The quantity inside parentheses in Eq. (2.39) strongly resembles the current density $\boldsymbol{j}(\boldsymbol{x}, t)$. For finite particles, it is *not* exactly the same, but as long as the particle dimensions are small compared to the length scale over which the field changes appreciably, the two will be indistinguishable from each other under the integral.[4] The result is that, for sufficiently small particles, we can write

$$W_{\text{el}} = \int_{t_1}^{t_2} dt \int_V d\boldsymbol{x}\, \boldsymbol{j}(\boldsymbol{x}, t) \cdot \boldsymbol{e}(\boldsymbol{x}, t), \tag{2.40}$$

effectively treating the particles as point charges under the integral, while regarding them as finite particles for the generation of the electric field $\boldsymbol{e}(\boldsymbol{x}, t)$.

Finally, we can use Ampere's law [Eq. (2.1d)] to eliminate the current density altogether, obtaining an expression

$$W_{\text{el}} = \frac{c}{4\pi} \int_{t_1}^{t_2} dt \int_V d\boldsymbol{x}\, \boldsymbol{e} \cdot \left(\nabla \times \boldsymbol{b} - \frac{1}{c} \frac{\partial \boldsymbol{e}}{\partial t} \right) \tag{2.41}$$

for the electrical work solely (if rather awkwardly) in terms of field quantities.

2.2.2   The Poynting Vector and Energy Density

Fortunately, the expression can be simplified considerably. The vector identity

$$\nabla \cdot (\boldsymbol{e} \times \boldsymbol{b}) = \boldsymbol{b} \cdot (\nabla \times \boldsymbol{e}) - \boldsymbol{e} \cdot (\nabla \times \boldsymbol{b}), \tag{2.42}$$

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[4] Strictly speaking, it is only the effective field, i.e., the electric field *minus* the Coulomb field of the nth particle that must vary slowly. The Coulomb field generated by a very small particle will certainly vary rapidly in space; but, by symmetry, this field can make no contribution to the force on the particle and is thus immaterial to the integral [Eq. (2.40).

allows us to rewrite the first term in parentheses as

$$e \cdot \nabla \times b = b \cdot (\nabla \times e) - \nabla \cdot (e \times b) \tag{2.43}$$

or, using the Maxwell-Faraday equation [Eq. (2.1c)],

$$e \cdot \nabla \times b = -\frac{1}{c} b \cdot \frac{\partial b}{\partial t} - \nabla \cdot (e \times b) . \tag{2.44}$$

Noting that (for any vector $a(t)$)

$$a \cdot \frac{\partial a}{\partial t} = \frac{1}{2} \frac{\partial \|a\|^2}{\partial t}, \tag{2.45}$$

this gives

$$W_{\text{el}} = -\int_{t_1}^{t_2} dt \int_V dx \left(\nabla \cdot S + \frac{\partial u}{\partial t} \right) \tag{2.46}$$

where

$$S(x, t) \equiv \frac{c}{4\pi} e \times b \tag{2.47}$$

is termed the *Poynting vector*, and

$$u(x, t) = \frac{1}{8\pi} \left(\|e\|^2 + \|b\|^2 \right) \tag{2.48}$$

is the *electromagnetic energy density*.

To understand this result physically, observe that if we choose the volume V to be large enough that the field has decayed to zero at the boundaries (i.e., large enough to "contain" both the particles and the field), then the $\nabla \cdot S$ term vanishes under integration by parts. In this case

$$W_{\text{el}} = -\int_{t_1}^{t_2} dt \int_V dx \frac{\partial u}{\partial t} = -[U(t_2) - U(t_1)] \tag{2.49}$$

where $U(t)$ is

$$U(t) = \int_V dx \, u(x, t). \tag{2.50}$$

Since W_{el} is the work performed *on* the material system *by* the field, it appears evident that U can be interpreted as the energy contained *in* the electromagnetic field (so that $-\Delta U$ is the energy being transferred from field to particles), and u as the corresponding energy density.

The interpretation of S is similarly facilitated by considering a volume V that contains no particles. In this case W_{el} is zero, and Eq. (2.46) becomes

$$0 = \int_{t_1}^{t_2} dt \int_V dx \left(\nabla \cdot S + \frac{\partial u}{\partial t} \right) \tag{2.51}$$

or after differentiating with respect to t_2 and letting the volume V tend to zero

$$\nabla \cdot \boldsymbol{S} + \frac{\partial u}{\partial t} = 0. \tag{2.52}$$

This equation has the form of a *continuity law*, indicating that – in the absence of interactions with charged particles – the total energy in the electromagnetic field is conserved. The Poynting vector may be understood as an energy current density, indicating the rate and direction of the flow of electromagnetic energy at a given point in space.

2.2.3 Experimental Detection of the Electromagnetic Field

An important consequence of these results is that it allows us to describe concretely how the electromagnetic field can be detected experimentally. Stationary electric or magnetic fields can, of course, be measured directly by their observed force effects on charged or magnetically active materials. Dynamic fields such as the propagating beams described in the last section are somewhat more difficult to quantify since the response times of even high-speed electronic devices are much longer than, for example, the rapid (femtosecond) oscillation time scales of visible radiation. Instead of tracking the field directly, however, detection of such high-frequency fields can be accomplished by measuring their stored electromagnetic energy.

One of the oldest devices for accomplishing this task is the *bolometer* or thermal detector. The operating principle of a bolometer is very simple. A small piece of strongly absorbing material is manufactured and placed in thermal contact with a sensitive thermometer and weak thermal contact with a heat reservoir. The optical response of the absorbing material must be sufficiently strong that essentially all electromagnetic energy impinging on it will be absorbed, i.e., transformed into kinetic and potential energy of the material particles. As radiation impinges on the detector, the associated increase of energy in the material leads to thermal heating which is detected by the thermometer. The thermal reservoir preserves thermal stability by allowing thermal energy to leave the sensor at a known rate. In this way, temperature change in the optical absorber provides a concrete metric for the energy content of the impinging electromagnetic field.

Using such a device, the magnitude of the elctromagnetic field may be measured in energetic terms – much more familiar to most of us than the charge/area units of the electromagnetic field itself. Let us examine two common metrics for the strength of the electromagnetic field, noting specifically their relation to the energy density u_{el} and the Poynting vector $\boldsymbol{S}$ just introduced.

First, suppose the electric field of interest is an ultrafast laser pulse, with a finite spatial extent in all three directions. In spectroscopy, such pulses are typically designed to mimic the ideal beams of Eq. (2.26), although in reality the finite spatial extent of the beam implies that their must be a continuous distribution of propagation vectors $\hat{s}$. Since the beam has finite dimensions in all three directions, the total energy contained in the beam

can be calculated as

$$U_{\text{pulse}} = \int d\boldsymbol{x}\, u(\boldsymbol{x}, t) = \frac{1}{8\pi} \int d\boldsymbol{x} \left(\|\boldsymbol{e}(\boldsymbol{x}, t)\|^2 + \|\boldsymbol{b}(\boldsymbol{x}, t)\|^2 \right), \tag{2.53}$$

where the integration volume must span the entire spatial extent of the beam. When we refer to the "pulse energy" of an ultrafast laser, it is this quantity that we mean.

On the other hand, consider the opposite regime of a continuous-wave laser or other source that produces a beam with a well-defined propagation axis $\hat{\boldsymbol{s}}$ but a stable amplitude, rather than a series of discrete pulses. In this case, it is meaningless to speak of the "energy" of the beam, since the field is continuously non-zero all the way from the source to the detector. We can, however, speak of the energy flux of the beam, termed the *irradiance*, i.e., the total amount of electromagnetic energy that passes through a given surface per unit time. For a flat surface, the irradiance is directly measured by the projection of the Poynting vector onto the surface normal. For an ideal beam of the form of Eq. (2.26), the Poynting vector takes the form

$$\boldsymbol{S}(\boldsymbol{x}, t) \equiv \frac{c}{4\pi} \boldsymbol{e} \times (\hat{\boldsymbol{s}} \times \boldsymbol{e}(\boldsymbol{x}, t)) = \frac{c}{4\pi} \hat{\boldsymbol{s}} \|\boldsymbol{e}(\boldsymbol{x}, t)\|^2. \tag{2.54}$$

and is thus parallel to the propagation axis $\hat{\boldsymbol{s}}$. The irradiance on a flat surface perpendicular to the propagation axis is then given exactly by the magnitude of the Poynting vector, although any real detector will actually measure the integrated quantity

$$\text{Ir}_{\text{det}} = \frac{c}{4\pi\tau_{\text{det}}A_{\text{det}}} \int_{t_o}^{t_o+\tau_{\text{det}}} dt \int dA\, \|\boldsymbol{e}(\boldsymbol{x}, t)\|^2, \tag{2.55}$$

where τ_{det} is a finite integration time set by the detector response and the integral dA extends over a finite surface of area A_{det} perpendicular to the propagation axis $\hat{\boldsymbol{s}}$.

Since the signal measured by the detector is thus determined by integrating the *intensity*

$$I(\boldsymbol{x}, t) = \frac{c}{8\pi} \|\boldsymbol{e}(\boldsymbol{x}, t)\|^2 \tag{2.56}$$

of the beam, we often use the intensity itself as a measure of the beam power. The word "intensity" should be used somewhat carefully, however, since in practice a variety of different measures of beam power are often referred to simply as the "intensity." In particular, we will also use the word "intensity" to describe the frequency-domain quantity

$$I(\boldsymbol{x}, \omega) = \frac{c}{8\pi} \|\breve{\boldsymbol{e}}(\boldsymbol{x}, \omega)\|^2. \tag{2.57}$$

If the detector response time τ_{det} is long relative to the oscillation frequency of the beam, the irradiance can equivalently be written as a frequency integral over $I(\omega)$ since

$$\begin{aligned}
\text{Ir}_{\text{det}} &= \frac{c}{16\pi^3 \tau_{\text{det}} A_{\text{det}}} \int dA \int d\omega \int d\omega'\, \breve{\boldsymbol{e}}(\boldsymbol{x}, \omega) \cdot \breve{\boldsymbol{e}}(\boldsymbol{x}, \omega') \int_{t_o}^{t_o+\tau_{\text{det}}} dt\, e^{-i(\omega+\omega')t} \\
&\approx \frac{c}{8\pi^2 \tau_{\text{det}} A_{\text{det}}} \int dA \int d\omega\, \breve{\boldsymbol{e}}(\boldsymbol{x}, \omega) \cdot \breve{\boldsymbol{e}}(\boldsymbol{x}, -\omega) \tag{2.58} \\
&= \frac{1}{\tau_{\text{det}} A_{\text{det}}} \int dA \int d\omega\, I(\boldsymbol{x}, \omega). \tag{2.59}
\end{aligned}$$

The frequency-domain intensity $I(\omega)$ is a particularly useful descriptor of the beam in frequency-resolved detection schemes such as interferometers or grating monochromators where the signal in a given frequency channel is directly proportional to $I(\omega)$.

2.3 Microscopic Electrodynamics

The results of the last section provide the complete solution to Maxwell's equations in vacuum. In the presence of charged particles, the behavior of the electric and magnetic fields is much more complex and cannot in general be solved analytically. In this section we first derive some general features of the electromagnetic field in point-particle systems and then investigate approximate solutions in two limiting cases.

2.3.1 The Inhomogeneous Wave Equation

To begin our investigation, we first recast Maxwell's equations into differential equation for the individual (electric or magnetic) fields. To this end, take the curl of the Maxwell-Faraday equation [Eq. (2.1c)] and use Ampere's law [Eq. (2.1d)] to eliminate the magnetic field. The result is:

$$\nabla \times (\nabla \times e) + \frac{1}{c^2}\frac{\partial}{\partial t}\left(4\pi j + \frac{\partial e}{\partial t}\right) = 0. \tag{2.60}$$

Next, expand the first term using the vector identity

$$\nabla \times (\nabla \times e) = \nabla\left(\nabla \cdot e\right) - \nabla^2 e \tag{2.61}$$

and use Gauss's law to replace $\nabla \cdot e$ with $4\pi\varrho$ to obtain

$$\frac{1}{c^2}\frac{\partial^2 e}{\partial t^2} - \nabla^2 e = -4\pi\nabla\varrho - \frac{4\pi}{c^2}\frac{\partial j}{\partial t}. \tag{2.62}$$

This yields a differential equation for the electric field in terms of the charge and current densities. A completely analogous derivation (taking the curl of Eq. (2.1d) and using Eqs. (2.1b) and (2.1c) to simplify) gives the parallel result

$$\frac{1}{c^2}\frac{\partial^2 b}{\partial t^2} - \nabla^2 b = \frac{4\pi}{c}\nabla \times j(x, t) \tag{2.63}$$

for the magnetic field.

Each vector component of Eqs. (2.62) and (2.63) has the form of the *inhomogeneous wave equation*

$$\frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2} - \nabla^2\psi = 4\pi f(x, t), \tag{2.64}$$

where the function $f(x, t)$ is called the *source* of the field $\psi(x, t)$. Such equations can be solved analytically, although since the derivation is rather tedious we defer it to Section (2.6). Here we only state the result:

$$\psi(x, t) = \int dx' \frac{f(x', t - |x - x'|/c)}{|x - x'|}. \tag{2.65}$$

Applying this solution to each component of Eqs. (2.62) and (2.63), the electric and magnetic fields can be solved *exactly* in terms of the "source" charge and current densities ϱ and j.

Before we explore these solutions in detail, however, let's take a moment to clarify what they represent. It is critical to recognize that the dynamics of the source fields ϱ and j are themselves influenced by e and b. As a result, neither Eq. (2.62) nor its solution [Eq. (2.66)] is sufficient to determine the field/particle dynamics: to use either one, we would first need to know the *exact* dynamics of the material system! Nonetheless, we will often be able to closely approximate a full solution by iteratively correcting the dynamics. For example, we might first study the particle dynamics under the influence of the "zeroth order" electromagnetic field (i.e., the field that would exist without any particles present) and then use the resulting material dynamics as sources for a new "first order" electric field via Eq. (2.66). In fact, the perturbation theory framework used for virtually all spectroscopic measurements is essentially just an iterative series of such approximations where the particle dynamics at each iteration "feel" the electric field determined by the previous step. When we speak of different "orders" of spectroscopy, we are generally referring to how many iterations of this process are required before a given experiment can be captured by the theory. Thus, although we cannot generally use Eq. (2.66) to generate exact answers, it is extremely useful to know in advance what its solutions look like for a given set of sources.

With this caveat, we proceed to apply the general solution [Eq. (2.65)] to the wave equations [Eq. (2.62) and (2.63)] to find that

$$e(x, t) = -\int dx' \frac{\nabla' \varrho(x', \tau)}{\|x - x'\|} - \frac{1}{c^2} \frac{\partial}{\partial t} \int dx' \frac{j(x', \tau)}{\|x - x'\|} \tag{2.66}$$

and

$$b(x, t) = \frac{1}{c} \int dx' \frac{\nabla' \times j(x', \tau)}{\|x - x'\|} \tag{2.67}$$

where

$$\tau = t - \frac{1}{c} \|x - x'\|. \tag{2.68}$$

In these expressions, we use the notation ∇' to indicate the gradient operator with respect to x', as opposed to the gradient ∇ with respect to x.

In the next section, we will see that these expressions can be brought into a simpler form. Already, however, they offer considerable physical insight. Notice in particular that

the charge and current densities are sampled not at the observation time t but at an earlier time τ determined by the distance $\|\boldsymbol{x} - \boldsymbol{x}'\|$ between the observation point $\boldsymbol{x}$ and the source point $\boldsymbol{x}'$. Physically, this means that *changes to the material densities ϱ and $\boldsymbol{j}$ can alter the electromagnetic field only after a finite propagation time determined by the distance from the source point and the speed of light.* This recognition that electromagnetic signals require a finite time to propagate through space was the key insight (due to Maxwell) that gave rise to our modern understanding of electrodynamics. Prior theories of electricity and magnetism had generally been built on the principle of "action at a distance." Changes to the configuration of particles at one point in space were instantaneously communicated to particles at other locations, no matter how widely separated. The elimination of such instantaneous processes in Maxwell's field theory revolutionized the contemporary understanding of electromagnetism and set the stage for further fundamental developments such as Einstein's theory of relativity.

2.3.2 The Scalar and Vector Potentials

To bring these results into a more concise form, it is helpful to eliminate the gradient operator ∇' inside the source integrals for $\boldsymbol{e}$ and $\boldsymbol{b}$. Let's focus on the electric field first. Using integration by parts, the first integral on the right hand side of Eq. (2.66) can be written

$$-\int d\boldsymbol{x}' \frac{\nabla' \varrho'(\boldsymbol{x}', \tau)}{\|\boldsymbol{x} - \boldsymbol{x}'\|} = \int d\boldsymbol{x}' \varrho'(\boldsymbol{x}', \tau) \nabla' \frac{1}{\|\boldsymbol{x} - \boldsymbol{x}'\|}. \tag{2.69}$$

(Note that $\|\boldsymbol{x} - \boldsymbol{x}'\|^{-1}$ decays to zero as $\boldsymbol{x}' \to \infty$.) Now, the argument $\|\boldsymbol{x} - \boldsymbol{x}'\|^{-1}$ of the gradient operators depends in exactly the same way on $-\boldsymbol{x}$ as it does on $\boldsymbol{x}'$ and, as a result,

$$\nabla' \frac{1}{\|\boldsymbol{x} - \boldsymbol{x}'\|} = -\nabla \frac{1}{\|\boldsymbol{x} - \boldsymbol{x}'\|}. \tag{2.70}$$

Plugging this back into Eq. (2.69) gives

$$-\int d\boldsymbol{x}' \frac{\nabla' \varrho'(\boldsymbol{x}', \tau)}{\|\boldsymbol{x} - \boldsymbol{x}'\|} = -\nabla \int d\boldsymbol{x}' \frac{\varrho'(\boldsymbol{x}', \tau)}{\|\boldsymbol{x} - \boldsymbol{x}'\|}. \tag{2.71}$$

Thus we have exchanged a gradient operator *inside* the integral for the overall gradient *of* the integral. An analogous series of operations for the source integral in Eq. (2.67) for the magnetic field gives

$$\frac{1}{c} \int d\boldsymbol{x}' \frac{\nabla' \times \boldsymbol{j}(\boldsymbol{x}', \tau)}{\|\boldsymbol{x} - \boldsymbol{x}'\|} = \nabla \times \left(\frac{1}{c} \int d\boldsymbol{x}' \frac{\boldsymbol{j}(\boldsymbol{x}', \tau)}{\|\boldsymbol{x} - \boldsymbol{x}'\|} \right) \tag{2.72}$$

With these results, Eqs. (2.66) and (2.67) can be rewritten

$$\boldsymbol{e}(\boldsymbol{x}, t) = -\nabla \phi(\boldsymbol{x}, t) - \frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} \tag{2.73}$$

$$\boldsymbol{b}(\boldsymbol{x}, t) = \nabla \times \boldsymbol{A}(\boldsymbol{x}, t) \tag{2.74}$$

in terms of a *scalar potential*

$$\phi(x,t) = \int dx' \frac{\varrho(x', t - \frac{1}{c}\|x - x'\|)}{\|x - x'\|} \tag{2.75}$$

and a *vector potential*

$$A(x,t) = \frac{1}{c} \int dx' \frac{j(x', t - \frac{1}{c}\|x - x'\|)}{\|x - x'\|}. \tag{2.76}$$

Note that Eqs. (2.75) and (2.76) involve only four independent quantities: the single component of ϕ and the three vector components of A. This is a significantly more condensed presentation of information in comparison to Eqs. (2.73) and (2.74) which involve *six* independent quantities (three components for each field). Partly for this reason, it is often more convenient in electrodynamics to work with the potentials A and ϕ rather than the fields they determine.

The other key advantage to working with potentials is that they allow for considerably more flexibility in performing calculations. Perhaps surprisingly, while A and ϕ uniquely determine e and b, the converse is not true: many different potentials can give rise to the same fields. Note, for example, that if ϕ and A were replaced in Eqs. (2.73) and (2.74) with the new potentials

$$A' = A + \nabla f(x,t) \tag{2.77}$$

$$\phi' = \phi - \frac{1}{c}\frac{\partial f}{\partial t} \tag{2.78}$$

the values of the fields would be left unchanged. (Check it!) A transformation of this sort is called a *gauge transformation*. A set of relations that (in addition to Maxwell's equations) uniquely determine A and ϕ is called a *gauge condition*. The potentials defined by Eqs. (2.75) and (2.76) correspond to a gauge condition known as the *Lorenz gauge*. The Lorenz gauge will be sufficient for our purposes in this text and (unless specifically noted), we will always take the potentials to be defined by Eqs. (2.73) and (2.74). Readers who wish to learn more about the general properties of the scalar and vector potentials can consult Section 2.5. This material is, however, unnecessary for any further developments in the text.

2.3.3 Near Field Electrodynamics: The Coulomb Potential

With these general observations in hand, let us examine the behavior of the field in close proximity to a set of point charges whose velocities are small relative to the speed of light. In this case, we can reasonably make the approximation $\tau = t - \frac{1}{c}\|x - x'\| \approx t$ in Eqs. (2.75) and (2.76), giving

$$\phi(x,t) = \int dx' \frac{\varrho(x', t)}{\|x - x'\|} \equiv \phi_{\mathrm{C}}(x,t) \tag{2.79}$$

and

$$A(x, t) = \frac{1}{c} \int dx' \frac{j(x', t)}{\|x - x'\|}. \tag{2.80}$$

The near-field scalar potential (2.79) is known as the *Coulomb potential*, and it dominates the electric field at short distances: note that A (and hence also $\frac{\partial A}{\partial t}$) scales as $1/\|x - r_n\|$, while $\nabla \phi$ scales as $1/\|x - r_n\|^2$. Moreover, for small velocities, the magnetic force on a charged particle (proportional to $\frac{v_n}{c}$) is usually negligible. For point particles (see Eq. (1.20)), the electromagnetic force [Eq. (1.24)] can thus be calculated directly from the Coulomb potential

$$\phi_C(x, t) = \sum_n \frac{q_n}{\|x - r_n\|} \tag{2.81}$$

as simply

$$F_n^{(EM)} \approx q_n e_n^{(eff)} \tag{2.82}$$

$$= q_n \sum_{m \neq n} q_m \frac{r_n - r_m}{|r_n - r_m|^3}. \tag{2.83}$$

This *Coulomb force* is the theoretical basis for molecular dynamics (MD) simulations. Since the magnetic field plays no role in Coulombic interactions, it (along with the vector potential) is often ignored completely in such treatments.

2.3.4 Far Field Electrodynamics: Spherical Waves

In contrast, let us now examine the behavior of the fields in the *far field* regime, i.e., at great distances from any sources. In particular, suppose that the charge and current densities are localized in a small region of space of radius R centered around the point x_0, so that $\varrho(x', t) = 0$ and $j(x', t) = 0$ whenever $\|x' - x_0\| > R$. We are interested in the behavior of the field at distances $\|x - x'\| \gg R$.

In this case, we can evaluate the potentials in a perturbative series in $\frac{1}{r}$ where

$$r = x - x_0. \tag{2.84}$$

Note carefully, however, that since the charge and current densities are evaluated at the retarded time $\tau = t - \frac{1}{c}\|x - x'\|$, this spatial expansion in large distance also implies a temporal expansion around the central retarded time

$$\tau_r = t - \frac{r}{c} \tag{2.85}$$

Indeed, defining

$$\delta r = x' - x_0, \tag{2.86}$$

the retarded time can be approximated as

$$\tau = t - \frac{\|\boldsymbol{r} - \delta\boldsymbol{r}\|}{c} \tag{2.87}$$

$$\approx t - \frac{r}{c} + \frac{\boldsymbol{r} \cdot \delta\boldsymbol{r}}{rc} + O\left(r^{-1}\right), \tag{2.88}$$

to zeroth order in $1/r$. Since the quantity $\|\boldsymbol{r} - \boldsymbol{r}_0\|^{-1}$ scales to lowest order as r^{-1}, Eqs. (2.75) and (2.76) become (to order r^{-1})

$$\phi(\boldsymbol{x}, t) = \int d\delta\boldsymbol{r} \frac{\varrho(\boldsymbol{x}_0 + \delta\boldsymbol{r}, t - \frac{1}{c}\|\boldsymbol{r} - \delta\boldsymbol{r}\|)}{\|\boldsymbol{r} - \delta\boldsymbol{r}\|} \tag{2.89}$$

$$\approx \frac{1}{r} \int d\boldsymbol{x}' \varrho(\boldsymbol{x}', \tau_r) + \frac{\boldsymbol{r}}{cr^2} \cdot \int d\boldsymbol{x}' \dot{\varrho}(\boldsymbol{x}', \tau_r)(\boldsymbol{x}' - \boldsymbol{x}_0) \tag{2.90}$$

and

$$\boldsymbol{A}(\boldsymbol{x}, t) \approx \frac{1}{cr} \int d\boldsymbol{x}' \boldsymbol{j}(\boldsymbol{x}', \tau_r) + \frac{\boldsymbol{r}}{c^2 r^2} \cdot \int d\boldsymbol{x}' \dot{\boldsymbol{j}}(\boldsymbol{x}', \tau_r)(\boldsymbol{x}' - \boldsymbol{x}_0). \tag{2.91}$$

For particle velocities small relative to the speed of light, the second term in Eq. (2.91) can be neglected thanks to its c^{-2} scaling. For the point-particle densities of Eqs. (1.20) and (1.21), we thus obtain

$$\phi(\boldsymbol{x}, t) \approx \frac{q_{\text{tot}}}{r} + \frac{\boldsymbol{r} \cdot \dot{\boldsymbol{\mu}}(\tau_r)}{cr^2} \tag{2.92}$$

and

$$\boldsymbol{A}(\boldsymbol{x}, t) \approx \frac{\dot{\boldsymbol{\mu}}(\tau_r)}{cr} \tag{2.93}$$

where we have defined the *total charge*

$$q_{\text{tot}} = \sum_n q_n \tag{2.94}$$

and the *dipole moment*

$$\boldsymbol{\mu}(t) = \sum_n q_n (\boldsymbol{r}_n - \boldsymbol{x}_0) \tag{2.95}$$

relative to $\boldsymbol{x}_0$.

It is particularly informative to examine the form of the field when the total charge vanishes. In this case, both scalar and vector potentials are determined by the dynamics of the dipole moment. Retaining as above only terms to lowest order in r^{-1} and c^{-1}, we obtain

$$e(\boldsymbol{x}, t) = \frac{\boldsymbol{r} \cdot \ddot{\boldsymbol{\mu}}(\tau_r)}{c^2 r^3} \boldsymbol{r} - \frac{\ddot{\boldsymbol{\mu}}(\tau_r)}{c^2 r} \tag{2.96}$$

$$b(\boldsymbol{x}, t) = \frac{\ddot{\boldsymbol{\mu}}(\tau_r) \times \boldsymbol{r}}{c^2 r^2}. \tag{2.97}$$

Note here that

$$b = -\frac{e \times r}{r}.$$ (2.98)

Conversely, the relation

$$e = \frac{b \times r}{r}$$ (2.99)

is easily verified using the vector identity

$$A \times (B \times C) = B(A \cdot C) - C(A \cdot B),$$ (2.100)

valid for arbitrary vectors A, B, C. Thus in the far-field region, *the electric and magnetic fields have the same magnitude (which decays as $1/r$), and the field polarizations are perpendicular to each other and to the position vector r.* Physically, these equations describe a *spherical wave* propagating out from the dipole at x_0. The frequency of the emitted wave or *electromagnetic radiation* is determined by the oscillation frequency (or frequencies) of the source dipole.

Equations 2.96 and 2.97 highlight an important fact concerning radiation; namely, radiation is generated by accelerating charges, as evidenced by the double time derivative of the dipole moment. A more general treatment would show that *any* accelerating charge produces an electromagnetic field that decays as r^{-1}, which has as a consequence electromagnetic energy being carried out to infinity. This means that radiation carries away kinetic and potential energy from the system, damping the motion of any accelerating charges, including oscillating dipoles. This is of fundamental importance in spectroscopy, where we typically call this radiation "fluorescence," when we consider where absorbed electromagnetic energy ends up.

2.4   Macroscopic Electrodynamics

In principle, Eqs. (2.1a) - (2.1d)], along with the Lorentz force law [Eq. (1.1)] and Newton's equations, provide an exact description of classical, *microscopic* field-particle dynamics. In practice, however, these equations are not very useful for describing spectroscopic experiments, which typically involve *macroscopic* samples, containing of the order of 10^{23} individual particles. Both the underlying equations *and* their solutions – if they could even be obtained – would be hopelessly complex. Yet despite this apparent complexity, we know from experience that spectroscopic measurements can often be described in terms of only a small number of intuitive parameters. For example, if the thermodynamic state (temperature, pressure, and volume) of a pure water sample is well-defined, we need not worry that its absorption spectrum will differ from one moment to the next, despite the fact that the microscopic structure is undoubtedly evolving rapidly.[5] This empirical

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[5]More accurately: if the spectrum does change, we must worry about our instrumentation (or what we're really trying to measure), not the sample!

observation suggests that it should be possible to derive from the microscopic equations a set of macroscopic electrodynamical equations that will more naturally and concisely describe spectroscopic measurements.

Conceptually, this microscopic to macroscopic transition strongly parallels the development of macroscopic thermodynamics from microscopic statistical mechanics. Just as the macroscopic pressure of a confined gas can be expressed as an average over an astronomically large number of particle/wall collisions, the *macroscopic fields* we see that spectroscopic experiments can be described in terms of macroscopic electric and magnetic fields, obtained by averaging the microscopic fields over a thermodynamic ensemble of different realizations of the system. It is critical to understand that such macroscopic fields will never be realized *exactly* in a spectroscopic experiment, just as it is virtually impossible that, at any given moment, the average force due to field-particle collisions will ever be *exactly* the thermodynamic pressure at *all* points on the surface of a gas cylinder. For macroscopic measurements, however – whether involving a photometer or a pressure gauge – macroscopic theories provide an essentially exact treatment.

2.4.1   Ensemble Averages

The starting point for our treatment is the distinction between physical microstates and macrostates. The *microstate* of a system consists of the positions and momenta of all material particles, along with the values of the electric and magnetic fields at all points in space. Needless to say, in the real world, it is virtually impossible to determine precisely the microstate of any system. Instead, we usually understand physical measurements in terms of system *macrostates*, collections of microstates that all give rise to the same, specified value of a small number of macroscopic parameters, e.g., temperature, pressure, volume, and perhaps the average value of the electric or magnetic fields (as measured by a macroscopic detector). In these terms, our goal is to convert the equations [Eqs. (2.1a) - (2.1d)] that describe the dynamics of field/particle microstates into a set of parallel equations that describe field/particle macrostates.

To this end, let us define, for any microscopic observable f, the *ensemble average*

$$\langle f \rangle_M = \sum_{\mu \in M} p_\mu^{(M)} f(\mu) \tag{2.101}$$

over all possible microstates μ consistent with a specified macrostate M. Here $p_\mu^{(M)}$ is the probability of observing the specific microstate μ in a system with macrostate M. For our present purposes, it will not be necessary to specify either the nature of the macrostate M or the method for determining the microstate probabilities $p_\mu^{(M)}$. Although we will later examine specific scenarios relevant to various spectroscopic measurements, the scope of the present discussion is quite broad.

In spectroscopy, we are primarily interested in the macroscopic electric and magnetic

fields

$$E(x, t) \equiv \langle e(x, t) \rangle_M \tag{2.102}$$

$$B(x, t) \equiv \langle b(x, t) \rangle_M . \tag{2.103}$$

In describing real spectroscopic measurements, we will refer almost exclusively to these quantities, rather than to the microscopic fields studied so far.

Since the ensemble average [Eq. (2.101)] is linear in the microscopic fields, and since each microscopic field satisfies Maxwell's microscopic equations [Eq. (2.1a) - (2.1d)], it is trivial to write down a set of formal relations

$$\nabla \cdot E = 4\pi \langle \varrho(x, t) \rangle_M \tag{2.104a}$$

$$\nabla \cdot B = 0 \tag{2.104b}$$

$$\nabla \times E + \frac{1}{c}\frac{\partial B}{\partial t} = 0 \tag{2.104c}$$

$$\nabla \times B - \frac{1}{c}\frac{\partial E}{\partial t} = \frac{4\pi}{c} \langle j(x, t) \rangle_M \tag{2.104d}$$

for the macroscopic fields in terms of the ensemble-averaged charge and current densities $\langle \varrho \rangle_M$ and $\langle J \rangle_M$. Unfortunately, these ensemble averaged densities are rather awkward to work with; to make these expressions useful, we must exchange these for quantities that are more physically intuitive *and* easier to calculate.

2.4.2   The Charge Density and Polarization Densities

Let's begin with the charge density. By definition [Eqs. (1.20) and (2.101)], we have

$$\langle \varrho(x, t) \rangle_M \equiv \sum_{\mu} p_{\mu}^{(M)} \sum_{n} q_n \delta \left(x - r_n^{(\mu)} \right) \tag{2.105}$$

where the index n runs over all ($\sim 10^{23}$) atoms in the system and where $r_n^{(\mu)}$ is the position of the nth particle in microstate μ. This rather abstract summation can be made more concrete by dividing it up into separate sums over (1) the number N_s of distinct *chemical species* in the system, (2) the number $N_{mol}^{(s)}$ of individual molecules (or chemical units) of species s, and (3) the number $N_{\text{p}}^{(s)}$ of individual number of particles composing a chemical unit of species s:

$$\langle \varrho(x, t) \rangle_M = \sum_{\mu} p_{\mu}^{(M)} \sum_{s=1}^{N_s} \sum_{n=1}^{N_{mol}^{(s)}} \sum_{i=1}^{N_{\text{p}}^{(s)}} q_i^{(s)} \delta \left(x - r_{sni}^{(\mu)} \right) . \tag{2.106}$$

The term "chemical species" here is intentionally broad; in molecular spectroscopy, these will usually be molecules, although ions, atoms, or even free valence electrons would be

equally valid.[6] In Eq. (2.106), $q_i^{(s)}$ is the charge on the ith particle in species s, while $r_{sni}^{(\mu)}$ is, in microstate *mu*, the position of the ith atom in the nth chemical unit of species s.

At first sight, this rather complicated indexing might not appear to be progress. The advantage is that this version can be rewritten as a simple summation over chemically intuitive quantities. Before simplifying, however, we introduce yet one more complication. Denote by $R_{sn}^{(\mu)}$ the center of mass of molecule n of species s in microstate μ. Noting that

$$\int dR\,\delta\left(R - R_{sn}^{(\mu)}\right) = 1 \qquad (2.107)$$

for any value of $R_{sn}^{(\mu)}$, the ensemble-averaged charge density can be written

$$\langle \varrho(x,t)\rangle_M = \sum_\mu p_\mu^{(M)} \sum_{s=1}^{N_{\text{s}}} \sum_{n=1}^{N_{\text{mol}}^{(s)}} \sum_{i=1}^{N_{\text{p}}^{(s)}} q_i^{(s)} \int dR\, \delta\left(R - R_{sn}^{(\mu)}\right) \delta\left(x - r_{sni}^{(\mu)}\right). \qquad (2.108)$$

After reordering the summation and integral signs, this becomes

$$\langle \varrho(x,t)\rangle_M = \sum_{s=1}^{N_{\text{s}}} \sum_{i=1}^{N_{\text{p}}^{(s)}} q_i^{(s)} \int dR\, p_{si}\left(R, x - R, t\right), \qquad (2.109)$$

where

$$p_{si}\left(R, \delta r, t\right) = \sum_\mu p_\mu^{(M)} \sum_{n=1}^{N_{\text{mol}}^{(s)}} \delta\left(R - R_{sn}^{(\mu)}\right) \delta\left(R + \delta r - r_{sni}^{(\mu)}\right) \qquad (2.110)$$

is the *joint probability density for finding a molecule of species s whose center of mass is at R and whose i^{th} particle is at $R + \delta r$.*

The key advantage to working with $p_{si}\left(R, \delta r\right)$ is that, since it is averaged over a macroscopic ensemble, it is expected to be a smooth function of the center-of-mass coordinate R, with variations occurring only over length scales much longer than a single molecule.[7] It is then appropriate to expand the probability density in a power series in its first argument. To this end, make the change of variables $\delta x = x - R$ to obtain

$$\langle \varrho(x,t)\rangle_M = \sum_{s=1}^{N_{\text{s}}} \sum_{i=1}^{N_{\text{p}}^{(s)}} q_i^{(s)} \int d\delta x\, p_{si}\left(x - \delta x, \delta x, t\right) \qquad (2.111)$$

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[6]Indeed, the grouping of a system into particular chemical species is not unique. It would never be incorrect, for example, to consider each particle in the system as a distinct "chemical species," although it would not be very useful.

[7]This assumption will be violated under the influence of coherent electromagnetic fields with wavelengths comparable to the molecular length scale, e.g., in coherent X-ray experiments.

and introduce the Taylor series expansion

$$p_{si}(\boldsymbol{x} - \delta\boldsymbol{x}, \delta\boldsymbol{x}, t) \approx p_{si}(\boldsymbol{x}, \delta\boldsymbol{x}, t) - \nabla p_{si}(\boldsymbol{x}, \delta\boldsymbol{x}, t) \cdot \delta\boldsymbol{x} + ... \tag{2.112}$$

Comparison with Eq. (2.111) prompts us to define the *macroscopic charge density*

$$\rho(\boldsymbol{x}, t) \equiv \sum_{s=1}^{N_{\mathrm{s}}} \sum_{i=1}^{N_{\mathrm{p}}^{(s)}} q_i^{(s)} \int d\delta\boldsymbol{x}\, p_{si}(\boldsymbol{x}, \delta\boldsymbol{x}, t) \tag{2.113}$$

$$= \sum_{s=1}^{N_{\mathrm{s}}} \sum_{\mu} p_\mu^{(M)} \sum_{n=1}^{N_{\mathrm{mol}}^{(s)}} \left(\sum_{i=1}^{N_{\mathrm{p}}^{(s)}} q_i^{(s)} \right) \delta\left(\boldsymbol{x} - \boldsymbol{R}_{sn}^{(\mu)}\right) \tag{2.114}$$

and the *polarization density*

$$\boldsymbol{P}(\boldsymbol{x}, t) = \sum_{s=1}^{N_{\mathrm{s}}} \sum_{i=1}^{N_{\mathrm{p}}^{(s)}} q_i^{(s)} \int d\delta\boldsymbol{x}\, p_{si}(\boldsymbol{x}, \delta\boldsymbol{x}, t)\, \delta\boldsymbol{x} \tag{2.115}$$

$$= \sum_{s=1}^{N_{\mathrm{s}}} \sum_{\mu} p_\mu^{(M)} \sum_{n=1}^{N_{\mathrm{mol}}^{(s)}} \sum_{i=1}^{N_{\mathrm{p}}^{(s)}} q_i^{(s)} \left(\boldsymbol{r}_{sni}^{(\mu)} - \boldsymbol{x} \right) \delta\left(\boldsymbol{x} - \boldsymbol{R}_{sn}^{(\mu)}\right) \tag{2.116}$$

so that

$$\langle \varrho(\boldsymbol{x}, t) \rangle_M \approx \rho(\boldsymbol{x}, t) - \nabla \cdot \boldsymbol{P}(\boldsymbol{x}, t) + ... \tag{2.117}$$

Note that any species consisting of single particles (e.g., atomic ions or free electrons) contribute only to the charge density ρ since the density $p_{si}(\boldsymbol{x}, \delta\boldsymbol{x}, t)$ must in this case be proportional to a delta function at $\delta\boldsymbol{x} = \boldsymbol{0}$. Neutral molecules, on the other hand, contribute *only* to the polarization density, while charged molecules contribute to both.

Physically, the macroscopic charge density $\rho(\boldsymbol{x}, t)$ represents an ensemble-averaged charge density if all chemical species are treated as indivisible units. In a system with only neutral molecules or with a homogeneous distribution of positive and negative ions, $\rho(\boldsymbol{x}, t)$ is identically zero. For real systems, the largest contribution to $\rho(\boldsymbol{x}, t)$ is typically from unbound electrons (e.g., valence electrons in a metal) which can move freely through the material in response to electromagnetic forces.

Recalling Eq. (2.95), on the other hand, we see that the polarization density is just the average dipole moment for species centered at $\boldsymbol{x}$. Physically, the fact that the polarization enters Maxwell's equations through the divergence $\nabla \cdot \boldsymbol{P}$ reflects the fact that variations in the (average) dipole moment across a sample correspond to a concentration of charge at individual points. For example, water molecules tend to orient themselves around charged species so that their molecular dipole moment is stabilized by the charge, e.g., with the negatively charged water oxygen atom pointing toward cations and away from anions. The result is a non-zero *divergence* for the polarization density (i.e., a change in the average dipole orientation) in the near vicinity of the ion, reflecting the concentration of partial charges from the polarized water molecules.

2.4.3 The Current Density

A completely analogous calculation for the current density gives the exact result

$$\langle j(x,t) \rangle_M = \sum_{s=1}^{N_s} \sum_{i=1}^{N_p^{(s)}} q_i^{(s)} \int d\delta x \, f_{si}(x - \delta x, \delta x, t), \qquad (2.118)$$

where

$$f_{si}(R, \delta r, t) = \sum_{\mu} p_{\mu}^{(M)} \sum_{n=1}^{N_{mol}^{(s)}} v_{sni}^{(\mu)} \delta\left(R - R_{sn}^{(\mu)}\right) \delta\left(R + \delta r - r_{sni}^{(\mu)}\right) \qquad (2.119)$$

is the flow density for the ith particle of species s. Parallel with our previous calculation, we could at this point carry out a Taylor series expansion for f_{si}. As it turns out, however, the zeroth order term already has the same overall magnitude as the polarization density $P(x)$. To zeroth order, we have

$$\langle j(x,t) \rangle_M = \sum_{s=1}^{N_s} \sum_{i=1}^{N_p^{(s)}} q_i^{(s)} \int d\delta x \, f_{si}(x, \delta x, t) \qquad (2.120)$$

$$= \sum_{s=1}^{N_s} \sum_{\mu} p_{\mu}^{(M)} \sum_{n=1}^{N_{mol}^{(s)}} \sum_{i=1}^{N_p^{(s)}} q_i^{(s)} v_{sni}^{(\mu)} \delta\left(x - R_{sn}^{(\mu)}\right). \qquad (2.121)$$

Comparison with Eq. (2.116) suggests that this quantity is closely connected to the polarization density. Indeed, the only difference is the replacement of the particle *displacements* with the particle *velocities*. In fact, using the chain rule to evaluate the derivative of Eq. (2.116) gives

$$\frac{\partial P(x)}{\partial t} = \sum_{s}^{\text{MP}} \sum_{\mu} p_{\mu}^{(M)} \sum_{n=1}^{N_{mol}^{(s)}} \sum_{i=1}^{N_p^{(s)}} q_i^{(s)} v_{sni}^{(\mu)} \delta\left(x - R_{sn}^{(\mu)}\right)$$

$$+ \sum_{s}^{\text{MP}} \sum_{\mu} p_{\mu}^{(M)} \sum_{n=1}^{N_{mol}^{(s)}} \sum_{i=1}^{N_p^{(s)}} q_i^{(s)} \left(r_{sni}^{(\mu)} - x\right) \frac{\partial}{\partial t} \delta\left(x - R_{sn}^{(\mu)}\right), \qquad (2.122)$$

where the text "MP" on the first summation symbol indicates that the sum extends over only "multi-particle" species. (Recall from the discussion following Eq. (2.116) that single-particle species do not contribute to the polarization density.) The first term here is exactly the contribution of multi-particle species to $\langle j \rangle_M$. The second term appears somewhat troublesome and indeed (like the delta function itself) has a well-defined mathematical meaning only after integration over a finite volume. Because the sum is restricted to multi-particle species, however, this term can, for most purposes, be neglected entirely. In real

systems, "multi-particle" species always contain at least one nuclear particle; as a result, the central coordinate $R_{sn}^{(\mu)}$ varies only slowly in time. Under the approximation that $R_{sn}^{(\mu)}$ is in fact static, the problematic term in Eq. (2.122) disappears, and we find that the multi-particle contribution to the ensemble-averaged current density is exactly the time derivative of the polarization density.

For single-particle species, we define the *macroscopic current density*

$$J(x, t) = \sum_{s}^{SP} \sum_{\mu} p_{\mu}^{(M)} \sum_{n=1}^{N_{\mathrm{mol}}^{(s)}} q^{(s)} v_{sn}^{(\mu)} \delta\left(x - R_{sn}^{(\mu)}\right), \tag{2.123}$$

i.e., just the average current density for single-particle species. Note the restriction "SP" for "single-particle" in the sum over species. With this definition, we have

$$\langle j(x, t) \rangle_M = J(x, t) + \frac{\partial P(x, t)}{\partial t}. \tag{2.124}$$

For most spectroscopic purposes, the sum over single-particle species can be further restricted to run only over unbound electrons since the velocities of atomic ions are orders of magnitude smaller than electronic velocities. These electronic "free charges" (sometimes, somewhat misleadingly, referred to as "true charges") are solely responsible for the macroscopic currents we measure, for example, with a voltmeter. In contrast, molecular and atomic charges are often termed "bound charges" since they are incapable of rapid, macroscopic displacement in response to electromagnetic forces.

2.5 The Scalar and Vector Potentials*

In Section 2.3.2, we encountered a representation of the electric and magnetic fields in terms of a pair of scalar and vector potentials. In this section, we explore the significance of these potentials in more detail, particularly their invariance under the gauge transformation [Eqs. (2.77) and (2.78)].

Mathematically, the representation of the electromagnetic fields in terms of scalar and vector potentials is grounded in the Helmholtz theorem. Although the basic content of the theorem has already been briefly stated in Section 3.3.1, we briefly review and rederive it here. Let $\tilde{E}(k, \omega)$ be an arbitrary (Fourier-transformed) field and consider the orthogonal components

$$\tilde{E}_{\parallel}(k, \omega) = k \frac{k \cdot \tilde{E}(k, \omega)}{k^2} \tag{2.125}$$

$$\tilde{E}_{\perp}(k, \omega) = -\frac{k \times \left(k \times \tilde{E}(k, \omega)\right)}{k^2}. \tag{2.126}$$

For each value of k, $E_{\parallel}$ is simply the projection of E along k, while $E_{\perp}$ is determined by the components of $\tilde{E}$ that are perpendicular to k. Together, these two quantities completely

determine the field. In fact, setting $A = B = k$ and $C = \tilde{E}$ in the generic vector identity

$$A \times (B \times C) = B\,(A \cdot C) - C\,(A \cdot B), \tag{2.127}$$

we see that

$$\tilde{E} = \tilde{E}_{\parallel} + \tilde{E}_{\perp}. \tag{2.128}$$

This equation is the essential result of the Helmholtz theorem: an arbitrary field in Fourier space can be decomposed uniquely into a *longitudinal* component $\tilde{E}_{\parallel}$ parallel to k and a *transverse* component orthogonal to k.

In real space, the relations $k \cdot \tilde{E}_{\perp} = 0$ and $k \times \tilde{E}_{\parallel} = 0$ implied by Eqs. (3.69) and (3.70) translate into (recall Eq. (2.17))

$$\nabla \times E_{\parallel}(x,t) = 0 \tag{2.129}$$
$$\nabla \cdot E_{\perp}(x,t) = 0. \tag{2.130}$$

Thus the Helmholtz theorem may alternatively be stated as the fact that an arbitrary field in real space may be uniquely decomposed as the sum of a vortex-free field $E_{\parallel}$ and a divergence-free field $E_{\perp}$.

It is useful to add to this finding a further observation regarding the general form of divergence- or vortex-free fields. In the first case, let $F(x,t)$ be an arbitrary vortex-free field. In Fourier space, the vortex-free condition $\nabla \times F = 0$ becomes simply $k \times F = 0$, implying that in the Helmholtz decomposition of F, only the longitudinal component $F_{\parallel}$ is non-zero. Now define a *scalar potential*

$$\tilde{\phi}(k,\omega) = -i\frac{k \cdot \tilde{F}(k,\omega)}{k^2} \tag{2.131}$$

and observe that, according to the Helmholtz decomposition

$$\tilde{F} = \tilde{F}_{\parallel} = -k\tilde{\phi}. \tag{2.132}$$

In real space this implies that

$$F(x,t) = -\nabla\phi(x,t). \tag{2.133}$$

Thus a vortex-free field can always be written as the gradient of a scalar potential.

On the other hand, suppose F is an arbitrary divergence-free field. In this case, only the transverse component $F_{\perp}$ is nonzero, and with

$$\tilde{A} = -i\frac{k \times \tilde{F}}{k^2} \tag{2.134}$$

we have

$$\tilde{F} = \tilde{F}_{\perp} = k \times \tilde{A}. \tag{2.135}$$

In real space, this implies that an arbitrary divergence-free field can always be written as the curl of a *vector potential* $\boldsymbol{A}(\boldsymbol{x}, t)$

$$\boldsymbol{F}(\boldsymbol{x}, t) = \nabla \times \boldsymbol{A}(\boldsymbol{x}, t). \tag{2.136}$$

So much for the mathematics. What does all this tell us about electromagnetic fields? According to Gauss's law for magnetism [Eq. (2.1b)], the magnetic field is always divergence-free and hence can be written as the curl

$$\boldsymbol{b} = \nabla \times \boldsymbol{A} \tag{2.137}$$

of a vector potential $\boldsymbol{A}(\boldsymbol{x}, t)$. Moreover, inserting this definition into the Maxwell-Faraday equation [Eq. (2.1c)] gives

$$\nabla \times \left(\boldsymbol{e} + \frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} \right) = 0, \tag{2.138}$$

implying that the quantity $\boldsymbol{e} + \frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t}$ is vortex-free and can be written as the gradient of a scalar potential ϕ, so that

$$\boldsymbol{e} = -\frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} - \nabla \phi. \tag{2.139}$$

Through Eqs. (2.137) and (2.139), the electric and magnetic fields are thus completely specified by the potentials $\boldsymbol{A}$ and ϕ.

Perhaps surprisingly, however, the converse is *not* true: the fields $\boldsymbol{e}$ and $\boldsymbol{b}$ do not uniquely determine the potentials $\boldsymbol{A}$ and ϕ. In fact, noting that $\nabla \times (\nabla f(\boldsymbol{x}, t))) = 0$ for any potential $f(\boldsymbol{x}, t)$, we see that the transformation

$$\boldsymbol{A} \to \boldsymbol{A} + \nabla f(\boldsymbol{x}, t) \tag{2.140}$$

leaves the magnetic field unchanged. If we simultaneously make the change

$$\phi \to \phi - \frac{1}{c} \frac{\partial f}{\partial t}, \tag{2.141}$$

the electric field $\boldsymbol{e}$ is also unchanged. Thus the potentials $\boldsymbol{A}$ and ϕ can be uniquely determined only after the introduction of additional constraints, beyond those imposed by Maxwell's equations. For this reason, the potentials $\boldsymbol{A}$ and ϕ should *not* be understood as physically meaningful themselves; it is only the fields $\boldsymbol{e}$ and $\boldsymbol{b}$ that have physical significance.

A change in the potentials according to Eqs. (2.140) and (2.141) is known as a *gauge transformation*. A set of constraints (in addition to Maxwell's equations) that uniquely determines $\boldsymbol{A}$ and ϕ is known as a *gauge*. The freedom to introduce gauge transformations is one of the great benefits of working with the potentials rather than with the fields $\boldsymbol{e}$ and $\boldsymbol{b}$ themselves since a judiciously chosen gauge can greatly simplify the solution of the corresponding differential equations. In the next sections we will explore two common choices of gauge.

2.5.1   The Coulomb Gauge

Perhaps the simplest way to uniquely specify the potentials is simply to set the longitudinal component $A_\parallel$ to zero, i.e., to impose the condition

$$\nabla \cdot A = 0. \tag{2.142}$$

Such a choice is always possible. In fact, let $A(x, t)$ and ϕ be *any* pair of vector and scalar potentials that give rise to the correct fields. According to the Helmholtz theorem, A can always be written as a sum

$$A = A_\perp - \nabla \phi_A \tag{2.143}$$

of a divergence-free component $A_\perp$ and the gradient of a scalar potential ϕ_A. If we set $f = \phi_A$ in the gauge transformation equations [Eq. (2.140)] and (2.141)], we obtain a new pair of potentials for which $\nabla \cdot A = 0$, as desired.

The chief advantage of the Coulomb gauge is that the potential ϕ is easy to calculate. In fact, substituting in the definition [Eq. (2.139)] into Gauss's law [Eq. (2.1a)] and noting the Coulomb gauge condition [Eq. (2.142)], we obtain

$$\nabla^2 \phi = -4\pi \rho(x, t). \tag{2.144}$$

This is the *Poisson equation* and yields the solution

$$\phi(x, t) = \int dx' \frac{\rho(x, t)}{\|x - x'\|}. \tag{2.145}$$

For stationary charges, the current density J vanishes, and it is easily verified that Maxwell's equations are satisfied by setting $A = 0$ and hence $b = 0$. Thus Coulomb potential alone completely specifies the electromagnetic field in the case of stationary charges.

For moving charges, however, the Coulomb potential is rather inconvenient since the differential equation for A (obtained from Ampere's law, [Eq. (2.1d)]) is difficult to analyze. In this case, it is more convenient to introduce another gauge condition known as the *Lorenz gauge*.

2.5.2   The Lorenz Gauge

The Lorenz gauge condition is chosen specifically to make the differential equations for both A and ϕ easier to solve. Introducing Eqs. (2.137) and (2.139) into Ampere's law [Eq. (2.1d)], we obtain

$$\nabla \times (\nabla \times A) + \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} + \nabla \frac{1}{c} \frac{\partial \phi}{\partial t} = \frac{4\pi}{c} J(x, t). \tag{2.146}$$

Expanding the first term using the identity

$$\nabla \times (\nabla \times A) = \nabla (\nabla \cdot A) - \nabla^2 A \tag{2.147}$$

gives

$$\nabla \left(\nabla \cdot \boldsymbol{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} \right) - \nabla^2 \boldsymbol{A} + \frac{1}{c^2} \frac{\partial^2 \boldsymbol{A}}{\partial t^2} = \frac{4\pi}{c} \boldsymbol{J}(\boldsymbol{x}, t). \tag{2.148}$$

The potential ϕ can be removed from this equation completely by requiring that the first term vanish, i.e., by imposing via a gauge transformation the *Lorenz gauge condition*

$$\nabla \cdot \boldsymbol{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} = 0. \tag{2.149}$$

(We will demonstrate shortly that there do in fact exist concrete gauge transformations from the Coulomb gauge that induce this condition.) In this case

$$\frac{1}{c^2} \frac{\partial^2 \boldsymbol{A}}{\partial t^2} - \nabla^2 \boldsymbol{A} = \frac{4\pi}{c} \boldsymbol{J}(\boldsymbol{x}, t). \tag{2.150}$$

This equation for $\boldsymbol{A}$ has the form of a *wave equation*, with the current density $\boldsymbol{J}$ acting as a source term.

Remarkably, an equation of nearly identical form can be obtained for the scalar potential under the Lorenz gauge. Inserting Eq. (2.139) into Gauss's law gives

$$-\nabla \cdot \left(\frac{1}{c} \frac{\partial \boldsymbol{A}}{\partial t} + \nabla \phi \right) = 4\pi \rho(\boldsymbol{x}, t) \tag{2.151}$$

or, under the Lorenz gauge condition [Eq. (2.149)],

$$\frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} - \nabla \phi = 4\pi \rho(\boldsymbol{x}, t) \tag{2.152}$$

Again, the differential equation for ϕ has the form of a wave equation, this time with the charge density ρ acting as the source.

Before proceeding further, let us confirm that it really is possible to enforce the Lorenz gauge condition [Eq. (2.149)] using a gauge transformation. Let $\boldsymbol{A}^{(C)}$ and $\phi^{(C)}$ be the Coulomb-gauge scalar and vector potentials. The Lorenz gauge condition is valid if we can find a scalar potential f such that

$$\boldsymbol{A} = \boldsymbol{A}^{(C)} + \nabla f \tag{2.153}$$

$$\phi = \phi^{(C)} - \frac{1}{c} \frac{\partial f}{\partial t} \tag{2.154}$$

and such that Eq. (2.149) is satisfied, i.e., such that

$$\nabla \cdot \left(\boldsymbol{A}^{(C)} + \nabla f \right) + \frac{1}{c} \frac{\partial}{\partial t} \left(\phi^{(C)} - \frac{1}{c} \frac{\partial f}{\partial t} \right) = 0. \tag{2.155}$$

Recalling that $\nabla \cdot \boldsymbol{A}^{(C)} = 0$, this again takes the form of a wave equation

$$\frac{1}{c^2} \frac{\partial^2 f}{\partial t^2} - \nabla^2 f = \frac{1}{c} \frac{\partial \phi^{(C)}}{\partial t}, \tag{2.156}$$

with the Coulomb potential itself acting as the source.

2.6   Solving the Wave Equation*

For readers interested in the explicit solutions, we in this section solve the generic inhomogeneous wave equation

$$\Box^2 \psi = f(\boldsymbol{x}, t) \tag{2.157}$$

where

$$\Box^2 = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2. \tag{2.158}$$

The wave equation occurs repeatedly in electrodynamics and has solutions that posses properties definitive of electromagnetic fields. In particular, we will see that the solutions *propagate* at the speed of light, c.

A particular solution to the wave equation may be found via the method of Green's functions. With this method, one finds the so-called Green's function solution which is defined by

$$\Box^2 G(\boldsymbol{x}, t, \boldsymbol{x}', t') = \delta(\boldsymbol{x} - \boldsymbol{x}')\delta(t - t'). \tag{2.159}$$

If such a function can be found, then the particular solution to Eq. 2.157 is given by

$$\psi(\boldsymbol{x}, t) = \iint \mathrm{d}\boldsymbol{x}'\mathrm{d}t' G(\boldsymbol{x}, t, \boldsymbol{x}', t') f(\boldsymbol{x}', t'). \tag{2.160}$$

Physically, the Green's function can be thought of as the field which is generated due to a point source localized at $\boldsymbol{x}'$ in space and at t' in time. Then, the solution given by Eq. 2.160 can be thought of as summing the contribution of all the point sources which comprise the physical source. To find the Green's function, we take the Fourier transform of Eq. 2.157 in time

$$\left(-\frac{\omega^2}{c^2} - \nabla^2\right)\tilde{G}(\boldsymbol{x}, \omega, \boldsymbol{x}', t') = \mathrm{e}^{\mathrm{i}\omega t'}\delta(\boldsymbol{x} - \boldsymbol{x}') \tag{2.161a}$$

If we make the definitions $k = \omega/c$ and $g(\boldsymbol{x}, \omega, \boldsymbol{x}', t') = \mathrm{e}^{-\mathrm{i}\omega t'}\tilde{G}(\boldsymbol{x}, \omega, \boldsymbol{x}', t')$, the equation can be somewhat simplified

$$(\nabla^2 + k^2)g(\boldsymbol{x}, \omega, \boldsymbol{x}', t') = -\delta(\boldsymbol{x} - \boldsymbol{x}') \tag{2.161b}$$

From hereon out, we confine ourselves to problems in which there are no boundary conditions other than the vanishing of fields as $|\boldsymbol{x}| \rightarrow \infty$. This ensures that g can only be a function of $|\boldsymbol{x} - \boldsymbol{x}'|$, the distance from the point source, affording us the opportunity to switch to a spherical coordinate system where $\boldsymbol{x}'$ is the origin. Since g depends only on r in this coordinate system, the angular derivatives in the Laplacian do not contribute and Eq. 2.161b reads

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(rg) + k^2 g = -\delta(r). \tag{2.162}$$

Everywhere except for $r = 0$, the right hand side is zero, so that the equation may be written as

$$\frac{\partial^2}{\partial r^2}(rg) + k^2(rg) = 0. \tag{2.163a}$$

This is a second-order homogeneous ordinary differential equation for rg which has the well know exponential solution

$$(rg) = Ae^{ikr} + Be^{-ikr}, \tag{2.163b}$$

such that

$$g = A\frac{e^{ikr}}{r} + B\frac{e^{-ikr}}{r}. \tag{2.163c}$$

In the limit that $r \rightarrow 0$, the delta function contributes, but the second term on the left-hand side of Eq. 2.162 becomes negligible compared to the first. So as $r \rightarrow 0$, we have

$$\nabla^2 g = -\delta(r). \tag{2.164}$$

To determine g, we note that formally, the Laplacian of $1/r$ is singular.[8] That is, we may write

$$\nabla^2 \frac{1}{r} = -4\pi\delta(r). \tag{2.165}$$

This implies that as g approaches zero, we have $g = 1/(4\pi r)$. This is already implicit in Eq. 2.163c provided that

$$A + B = \frac{1}{4\pi}. \tag{2.166}$$

We may now retrieve the Green's function using the definitions from above. Multiplying g by $e^{i\omega t'}$ and inverse Fourier transforming gives

$$G(r, t, t') = \frac{1}{2\pi} \int d\omega e^{-i\omega t} \left(A\frac{e^{i(t'+r/c)\omega}}{r} + B\frac{e^{i(t'-r/c)\omega}}{r} \right), \tag{2.167}$$

which can easily be integrated

$$G(r, t, t') = A\frac{\delta(t' + r/c - t)}{r} + B\frac{\delta(t' - r/c - t)}{r}. \tag{2.168}$$

The two solutions given by Eq. 2.168 provide two very different physical pictures of the response of the field to a localized source. The first term is called the retarded Green's function, G^+, and the second, the advanced Green's function, G^-

$$G^+(r, t, t') = \frac{\delta(t - t' - r/c)}{r}, \tag{2.169a}$$

$$G^-(r, t, t') = \frac{\delta(t - t' + r/c)}{r}. \tag{2.169b}$$

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[8]See appendix C.

To see what kind of behavior of the fields these functions give rise to, we change the time variable to $\tau = t - t'$ which means that the source is localized in time at $\tau = 0$ and in space at $r = 0$. We first consider the retarded Green's function, G^+. At $\tau = 0$, the instant when the source exists, the retarded Green's function is zero everywhere except $r = 0$. If τ is larger than zero, we see that the Green's function is zero everywhere except at the position $r = c\tau$. This implies that a disturbance localized at the origin spherically propagates outwards with velocity c. If τ is smaller than zero, (that is, we are considering times before the source existed) then the Green's function is zero everywhere since negative values of r are not allowed, by our definition of the coordinate system. On the other hand, the advanced Green's function is only non-zero *before* the source existed. This is a non-causal solution to Maxwell's equations and is clearly unphysical. We therefore reject it ($B = 0$) so that the actual Green's function for the wave equation is

$$G(|\boldsymbol{x} - \boldsymbol{x}'|, t - t') = \frac{\delta(t - t' - |\boldsymbol{x} - \boldsymbol{x}'|/c)}{4\pi|\boldsymbol{x} - \boldsymbol{x}'|}. \tag{2.170}$$

For an arbitrary source $f(\boldsymbol{x}, t)$, we may use Eq. 2.160 to find the solution

$$\psi(\boldsymbol{x}, t) = \frac{1}{4\pi} \iint d\boldsymbol{x}' dt' \delta(t - t' - |\boldsymbol{x} - \boldsymbol{x}'|/c) \frac{f(x', t')}{|\boldsymbol{x} - \boldsymbol{x}'|} = \frac{1}{4\pi} \int d\boldsymbol{x}' \frac{f(\boldsymbol{x}', t - |\boldsymbol{x} - \boldsymbol{x}'|/c)}{|\boldsymbol{x} - \boldsymbol{x}'|}.$$
$$\tag{2.171}$$

Equation 2.171 is the form of the solution to either the scalar or vector potential in the Lorentz gauge, provided that the source f is either the charge density or the current density, respectively. The form of the Green's function ensures that the time dependence of either the scalar or vector field is always retarded by an amount which depends on the distance between the source and the observation point. This is what was meant by the solutions "propagating" at the speed of light. Since the potentials have this behavior, the fields will as well.

Chapter 3

Spectroscopy and Material Response

3.1 Maxwell's Equations and Material Response

Finally, inserting these results into Eqs. (2.104a) - (2.104d), we obtain a set of macroscopic equations

$$\nabla \cdot \boldsymbol{E} = 4\pi\rho(\boldsymbol{x}, t) - 4\pi\nabla \cdot \boldsymbol{P}(\boldsymbol{x}, t) \tag{3.1a}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{3.1b}$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{3.1c}$$

$$\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t} = \frac{4\pi}{c}\boldsymbol{J}(\boldsymbol{x}, t) + \frac{4\pi}{c}\frac{\partial \boldsymbol{P}(\boldsymbol{x}, t)}{\partial t} \tag{3.1d}$$

that describe the dynamics of the macroscopic fields $\boldsymbol{E}$ and $\boldsymbol{B}$ in terms of the macroscopic charge, current, and polarization densities ρ, $\boldsymbol{J}$, and $\boldsymbol{P}$. For these equations to be useful, however, we must answer one additional question: How do the material densities respond to the electromagnetic field?

Fundamentally, answering this question is the sole purpose of molecular spectroscopy[1] and occupies most of the remaining material in this text. To simplify matters, however, we will limit our scope to the study of *homogeneous dielectric materials*, i.e., materials for that lack free charges and contain a uniform distribution of each chemical species. In this case, both the macroscopic charge and current densities vanish, so that we need consider only the coupling of the polarization density $\boldsymbol{P}(\boldsymbol{x}, t)$ to the electromagnetic field. Although any detailed calculation of the polarization will depend on the specific material being studied, a great deal can be learned from basic physical and mathematical principles.

3.1.1 Physical Considerations

At the outset, observe that, since $\boldsymbol{P}$ is a macroscopic quantity, it must depend only on the macroscopic fields $\boldsymbol{E}$ and $\boldsymbol{B}$; variations due to fluctuations in the microscopic fields $\boldsymbol{e}$ and

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[1]Although usually, of course, we also hope to learn something interesting about the material as a result!

b must sum to zero in the ensemble average. We can thus consider P to be a *functional* of the macroscopic fields $E(x, t)$ and $B(x, t)$. In mathematics, the word "functional" means a mapping from one function to another. Just as a "function" maps one set of variables (perhaps x and t) to another variable (perhaps E and B), a "functional" maps one function (in our case E and B) to another function (in our case P). The dependence of a functional on its arguments is usually represented by square brackets, i.e., the notation

$$P(x, t) = P[E(x', t'), B(x', t')] \tag{3.2}$$

indicates that the polarization field $P(x, t)$ is determined by the electric and magnetic fields $E(x', t')$ and $B(x', t')$. Note that the dependence of P on E and B need *not* be local in either space or time: the value of P at a given location x and time t may, in principle, depend on the values of the fields at any space-time point (x', t').

Relation [Eq. (3.2)] may seem hopelessly general, but physical intuition quickly guides us to a more concrete representation. First, recall that field-particle interactions are governed microscopically by the Lorentz force law [Eq. (1.1)], where the force due to the magnetic field is proportional to the ratio $\frac{v_n}{c}$. For most materials, the velocity of the individually particles is much smaller than the speed of light, and, as a result, the force exerted by the magnetic field is orders of magnitude weaker than that due to the electric field. At the macroscopic level, this suggests that, to a first approximation, we can neglect the dependence of P on the magnetic field entirely, so that Eq. (3.2) is replaced by

$$P(x, t) = P[E(x', t')]. \tag{3.3}$$

As it turns out, this approximation works extremely well for optical and infrared spectroscopy, and we will adopt it uniformly throughout the following text.

Second, note (again from the Lorentz force law) that field-particle interactions are local in space at the microscopic level. Any dependence of $P(x, t)$ on the value of the fields at other locations x' in space must therefore result from the macroscopic communication (through purely material means) of field-particle interactions across macroscopic distances. For example, the polarization of a molecular beam by a strong laser field at one point x' along its path will coherently carry that polarization along with it to other points x', until orientational diffusion and collisions between the gas molecules eventually destroy it. Apart from such tightly-controlled scenarios, however, collision-induced dephasing in most materials is too strongly to allow for the coherent transport required for nonlocal spatial response. From this point forward, we thus assume that the polarization $P(x, t)$ depends only on the (spatially) local field $E(x, t')$. Since the spatial variables x and x' are always understood to be the same for both P and E, they can be suppressed in our notation, so that Eq. (3.3) becomes

$$P(t) = P[E(t')]. \tag{3.4}$$

In contrast, the dependence of P is, for most materials, very much nonlocal in time. Recall, however, that physics is *causal*: the dynamics of a system are determined exclusively

by its past, never by its future. We thus expect that $P(x, t)$ is determined only by the value of E at times $t' \leq t$, i.e.,

$$P(t) = P[E(t' \leq t)]. \tag{3.5}$$

Finally, we expect the functional dependence of P on E to be *stable* in time. Specifically,

1. There ought to be some short time scale δt *below* which variations in the field no longer have any significant impact on the polarization and

2. There ought to be some long time scale T *beyond* which the system no longer "remembers" what the field looked like at earlier times.

Suppose, for example, that we design an experiment to sample the field at a series of $N = \frac{T}{\delta t}$ equally-spaced time points

$$t_n = t - T + n\delta t, \tag{3.6}$$

so that $t_N = t$. If we choose T to be far enough in the past and the spacing δt between sample points to be small enough, we expect that the discrete set of values $E_J(t_n)$ should be sufficient to determine the polarization. (The index J here runs over the three Cartesian coordinates x, y, z for the field polarization.) Mathematically, this means that each component $P_I(t)$ of the polarization vector can be expressed as some function

$$P_I(t) \approx f_I(E_x(t_0), E_y(t_0), E_z(t_0), E_x(t_1), ..., E_z(t_N); t, \delta t, T) \tag{3.7}$$

of the $3N$ discrete variables $E_J(t_n)$. Here the appearance of t, δt, and T acknowledges that the particular functional form f_I will depend on the set of sample points we have chosen for the field and (possibly) on the absolute time. Note that, since real-world measurements always involve a finite number of samples, if this assumption were *not* true, it would imply that no physical measurement on the field would ever be sufficient to determine the polarization!

3.1.2 Mathematical Formulation: Response Theory

Under these physical assumptions, it is straightforward to develop a more mathematically useful representation for the functional dependence of the polarization on the field. Recall that any analytic function $g(x_1, ..., x_N)$ of a set of discrete variables $x_1, ..., x_N$ can be expanded in a Taylor series

$$\begin{aligned}
g(x_1, ..., x_N) = {} & g(0, ..., 0) \\
& + \left.\frac{\partial g}{\partial x_1}\right|_{x=0} x_1 + \left.\frac{\partial g}{\partial x_2}\right|_{x=0} x_2 + ... + \left.\frac{\partial g}{\partial x_N}\right|_{x=0} x_N \\
& + \frac{1}{2!}\left.\frac{\partial^2 g}{\partial x_1^2}\right|_{x=0} x_1^2 + \left.\frac{\partial g}{\partial x_1 \partial x_2}\right|_{v=0} x_1 x_2 + ... + \frac{1}{2!}\left.\frac{\partial^2 g}{\partial x_N^2}\right|_{x=0} x_N^2 \\
& + \frac{1}{3!}\left.\frac{\partial^3 g}{\partial x_1^3}\right|_{x=0} x_1^3 + ...
\end{aligned} \tag{3.8}$$

around the value $\boldsymbol{x} = (x_1, ..., x_N) = \boldsymbol{0}$. Regarding the field values $E_J(t_n)$ as variables, this suggests that, for any fixed set of time points, Eq. (3.7) can be expanded in a Taylor series around the zero-field polarization:

$$
\begin{aligned}
P_I(t) \approx\ & f_I(0, ..., 0; t, \delta t, T) \\
& + \left.\frac{\partial f_I}{\partial E_x(t_0)}\right|_{E=0}^{t,\delta t,T} E_x(t_0) + ... + \left.\frac{\partial f_I}{\partial E_z(t_N)}\right|_{E=0}^{t,\delta t,T} E_z(t_N) \\
& + \frac{1}{2!} \left.\frac{\partial^2 f_I}{\partial [E_x(t_0)]^2}\right|_{E=0}^{t,\delta t,T} [E_x(t_0)]^2 + \left.\frac{\partial^2 f_I}{\partial E_x(t_0)\partial E_y(t_0)}\right|_{E=0}^{t,\delta t,T} E_x(t_0)E_y(t_0) + ... \\
& + \frac{1}{3!} \left.\frac{\partial^3 f_I}{\partial [E_x(t_o)]^3}\right|_{E=0}^{t,\delta t,T} [E_x(t_o)]^3 + ...,
\end{aligned}
\tag{3.9}
$$

where each line involves terms that scale with increasing powers of the field.

Let us focus now on the second line of Eq. (3.7), i.e., the contribution

$$
P_I^{(1)}(t) = \left.\frac{\partial f_I}{\partial E_x(t_0)}\right|_{E=0}^{t,\delta t,T} E_x(t_0) + ... + \left.\frac{\partial f_I}{\partial E_z(t_N)}\right|_{E=0}^{t,\delta t,T} E_z(t_N)
\tag{3.10}
$$

from all terms that are overall linear in the field values $E_J(t_n)$. These terms depend on a discrete set of $3N$ quantities

$$
\left.\frac{\partial f_I}{\partial E_x(t_0)}\right|_{E=0}^{t,\delta t,T}, ..., \left.\frac{\partial f_I}{\partial E_z(t_N)}\right|_{E=0}^{t,\delta t,T}
\tag{3.11}
$$

that are, by assumption, intrinsic properties of the material system at time t, aside from their parametric dependence on δt and T. Now, under the stability assumption of the last section, the polarization should be independent of our particular choice of δt so long as it is sufficiently small. For fixed T, this implies that the *magnitudes* of the expansion coefficients must scale linearly with δt

$$
\left.\frac{\partial f_I}{\partial E_x(t' < t)}\right|_{E=0}^{t,\delta t,T} \propto \delta t,
\tag{3.12}
$$

since the total *number* of such coefficients scales as $\frac{1}{\delta t}$ while the magnitude of the polarization is independent of δt. Further, since the response ought not to depend strongly on the specific choice of the sample points, the values of adjacent coefficients (say $\left.\frac{\partial f_I}{\partial E_x(t')}\right|_{E=0}^{t,\delta t,T}$ and $\left.\frac{\partial f_I}{\partial E_x(t'+\delta t)}\right|_{E=0}^{t,\delta t,T}$) must converge in the limit that $\delta t \to 0$. Finally, this implies that there must exist a function

$$
R_{JI}^{(1)}(t, t') = \lim_{\delta t \to 0} \frac{1}{\delta t} \left.\frac{\partial f_I}{\partial E_x(t')}\right|_{E=0}^{t,\delta t,T},
\tag{3.13}
$$

which completely characterizes the first order polarization vector. In terms of this function, the first-order polarization can be written

$$P_I^{(1)}(t) = \sum_n \delta t R_{JI}^{(1)}(t, t_n) E_J(t_n). \tag{3.14}$$

But this last expression is exactly the Riemann sum for the integral

$$\int_{t-T}^{t} dt' R_{JI}^{(1)}(t, t') E_J(t') \equiv \lim_{\delta t \to 0} \sum_n \delta t R_{JI}^{(1)}(t, t - T + n\delta t) E_J(t - T + n\delta t). \tag{3.15}$$

Moreover, since under our stability assumptions, the time interval T may be made arbitrarily large without changing the value of $P_I^{(1)}$, we have the exact result

$$P_I^{(1)}(t) = \sum_J \int_{-\infty}^{t} dt' R_{JI}^{(1)}(t, t') E_J(t'). \tag{3.16}$$

Applying exactly the same analysis to each line of Eq. (3.7), we find that the total polarization can be written

$$\boldsymbol{P}(t) = \sum_{n=0}^{\infty} \boldsymbol{P}^{(n)}(t) \tag{3.17}$$

where $\boldsymbol{P}^{(0)}$ is the polarization of the sample in the absence of any macroscopic field, and for $n \geq 1$

$$P_\alpha^{(n)}(t) = \sum_{\alpha_1,\ldots,\alpha_n} \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_{n-1} \ldots \int_{-\infty}^{t_2} dt_1 E_{\alpha_1}(t_1) E_{\alpha_2}(t_2) \ldots E_{\alpha_n}(t_n)$$
$$\times R_{\alpha_1 \ldots \alpha_n \alpha}^{(n)}(t, t_n, t_{n-1}, \ldots, t_1), \tag{3.18}$$

where $R_{\alpha_1 \ldots \alpha_n \alpha}^{(n)}(t, t_n, t_{n-1}, \ldots, t_1)$ is termed the nth-*order response function* for the polarization.

3.1.3   Tensors Transformations, Symmetry, and Invariance

Since the response functions $R_{\alpha_1 \ldots \alpha_n \alpha}^{(n)}(t, t_n, t_{n-1}, \ldots, t_1)$ are intrinsic properties of the material – independent of the field – they must satisfy any symmetry properties that the material itself possesses. This observation, sometimes know as the Von Neumann principle, is of great utility in molecular spectroscopy, and we stop here to consider some of its most important implications.

First, all material systems considered in this text will satisfy *time translation invariance*, i.e., the properties of the system are not changed by introducing an overall shift $t \to t + \delta t$ to the time axis. This at once implies that the response functions can depend only on the time *intervals* $t - t_m$, rather than on the absolute integration times t_m in Eq. (3.18). For

such systems, the response function can always be assumed to have the functional form $R^{(n)}_{\alpha_1...\alpha_n\alpha}(t - t_n, t_n - t_{n-1}, ..., t_2 - t_1)$. Defining $\tau_m = t_{m+1} - t_m$ (with $\tau_n = t - t_n$), the nonlinear polarization can be written

$$P^{(n)}_\alpha(t) = \sum_{\alpha_1,...,\alpha_n} \int_0^\infty d\tau_n ... \int_0^\infty d\tau_1 R^{(n)}_{\alpha_1...\alpha_n\alpha}(\tau_1, ..., \tau_n) \tag{3.19}$$

$$\times E_{\alpha_1}(t - \tau_1 - ... - \tau_n)E_{\alpha_2}(t - \tau_2 - ... - \tau_n)...E_{\alpha_n}(t - \tau_n).$$

Defining the response tensor to be zero for negative time delays (any $\tau_m < 0$), the integration limits can be extended to negative infinity to give

$$P^{(n)}_\alpha(t) = \sum_{\alpha_1,...,\alpha_n} \int_{-\infty}^\infty d\tau_n ... \int_{-\infty}^\infty d\tau_1 R^{(n)}_{\alpha_1...\alpha_n\alpha}(\tau_1, ..., \tau_n) \tag{3.20}$$

$$\times E_{\alpha_1}(t - \tau_1 - ... - \tau_n)E_{\alpha_2}(t - \tau_2 - ... - \tau_n)...E_{\alpha_n}(t - \tau_n).$$

This form will be assumed throughout the remainder of the text.

Second, any spatial symmetries present in the sample must also be reflected in the response function. The reason such symmetry relations are so powerful is that they may be combined with the general transformation laws for tensor quantities like $R^{(n)}_{\alpha_1...\alpha_n\alpha}$. Before exploring such symmetry relations, it is worth clarifying in more detail what exactly the term "tensor" means here. Strictly speaking, a *tensor* is any quantity $T_{\alpha_1...\alpha_n}$ that obeys the transformation relation

$$T'_{\alpha_1...\alpha_n} = \sum_{\beta_1,...,\beta_n} u_{\alpha_1\beta_1}...u_{\alpha_n\beta_n}T_{\beta_1...\beta_n} \tag{3.21}$$

whenever the coordinate system undergoes a transformation such that the position vector $\boldsymbol{x}$ is mapped to the transformed vector $\boldsymbol{x}'$ with components

$$x'_\alpha = \sum_\beta u_{\alpha\beta}x_\beta. \tag{3.22}$$

Here $\boldsymbol{u}$ is some unitary transformation matrix that satisfies the orthonormality condition

$$\sum_\alpha u_{\alpha\beta}u_{\alpha\gamma} = \delta_{\beta\gamma}. \tag{3.23}$$

Essentially, what Eq. (3.21) says is that each *component* of a tensor transforms like a vector.

That $R^{(n)}_{\alpha_1...\alpha_n\alpha}$ indeed obeys this transformation law follows from the vector transformation equations for $\boldsymbol{P}$ and $\boldsymbol{E}$. Under the coordinate transformation of Eq. (3.22), they transform as

$$P'_\alpha = \sum_\beta u_{\alpha\beta}P_\beta \tag{3.24}$$

$$E'_\alpha = u_{\alpha\beta}E_\beta. \tag{3.25}$$

Now, in the transformed reference frame, Eq. (3.19) reads

$$\left[P_\alpha^{(n)}\right]'(t) = \sum_{\alpha_1,...,\alpha_n} \int_{-\infty}^{\infty} d\tau_n ... \int_{-\infty}^{\infty} d\tau_1 \left[R_{\alpha_1...\alpha_n\alpha}^{(n)}\right]'(\tau_1, ..., \tau_n) \tag{3.26}$$

$$\times E'_{\alpha_1}(t - \tau_1 - ... - \tau_n) E'_{\alpha_2}(t - \tau_2 - ... - \tau_n) ... E'_{\alpha_n}(t - \tau_n)$$

or, in light of Eqs. (3.24) and (3.25),

$$\sum_\beta u_{\alpha\beta} P_\beta^{(n)}(t) = \sum_{\beta_1,...,\beta_n} \sum_{\alpha_1,...,\alpha_n} \int_{-\infty}^{\infty} d\tau_n ... \int_{-\infty}^{\infty} d\tau_1 \tag{3.27}$$

$$\times u_{\alpha_1\beta_1} ... u_{\alpha_n\beta_n} \left[R_{\alpha_1...\alpha_n\alpha}^{(n)}\right]'(\tau_1, ..., \tau_n)$$

$$\times E_{\beta_1}(t - \tau_1 - ... - \tau_n) E_{\beta_2}(t - \tau_2 - ... - \tau_n) ... E_{\beta_n}(t - \tau_n).$$

Multiplying both sides by $u_{\alpha\beta}$, summing over α, and applying Eq. (3.23) gives

$$P_\beta^{(n)}(t) = \sum_{\beta_1,...,\beta_n} \sum_{\alpha_1,...,\alpha_n,\alpha} u_{\alpha_1\beta_1} ... u_{\alpha_n\beta_n} u_{\alpha\beta} \int_{-\infty}^{\infty} d\tau_n ... \int_{-\infty}^{\infty} d\tau_1 \left[R_{\alpha_1...\alpha_n\alpha}^{(n)}(\tau_1, ..., \tau_n)\right]'$$

$$\times E_{\beta_1}(t - \tau_1 - ... - \tau_n) E_{\beta_2}(t - \tau_2 - ... - \tau_n) ... E_{\beta_n}(t - \tau_n). \tag{3.28}$$

Apart from relabeling the indices, however, this is simply the response theory equation [Eq. (3.19)] in the original (untransformed) reference frame, implying that

$$R_{\beta_1...\beta_n\beta}^{(n)}(\tau_1, ..., \tau_n) = \sum_{\alpha_1,...,\alpha_n,\alpha} u_{\alpha_1\beta_1} ... u_{\alpha_n\beta_n} u_{\alpha\beta} \left[R_{\alpha_1...\alpha_n\alpha}^{(n)}\right]'(\tau_1, ..., \tau_n). \tag{3.29}$$

This, finally, is exactly the tensor transformation law [Eq. (3.21)], albeit for the backward transformation $x' \to x$. The forward law can be obtained by repeatedly applying the transformation matrix u to both sides of the equation and using Eq. (3.23). Thus, our response functions really do transform as tensor quantities.

To see how the tensor transformation relation [Eq. (3.21)] can be combined with material symmetry properties, consider the specific example of *isotropic media*, i.e., materials whose macroscopic properties are unchanged by *all* symmetry transformation. In such systems, *inversion* of any axis via any one or more of the exchanges

$$x \to -x \tag{3.30}$$

$$y \to -y \tag{3.31}$$

$$z \to -z \tag{3.32}$$

must leave unchanged any macroscopic system properties – including the response functions. The same result holds for the *exchange* of any two axes via rotation and reflection of the system

$$x \leftrightarrow y \tag{3.33}$$

$$x \leftrightarrow z \tag{3.34}$$

$$y \leftrightarrow z. \tag{3.35}$$

These properties lead to symmetry relations between the response tensor elements such as

$$R_{xy}^{(1)} = R_{yx}^{(1)} \tag{3.36}$$

resulting from the exchange of x and y axes or

$$R_{xy} = R_{x(-y)} \tag{3.37}$$

corresponding to inversion of the y axis. Such symmetry relations drastically simplify the spectroscopic analysis of isotropic media.

For example, consider what happens to the response tensor element $R_{xy}^{(1)}$ when the y axis is inverted, corresponding to the unitary transformation matrix

$$\boldsymbol{u} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.38}$$

The tensor transformation law [Eq. (3.21)] implies that

$$\left[R_{xy}^{(1)}\right]' = -R_{xy}^{(1)}. \tag{3.39}$$

But the symmetry relation [Eq. (3.37)] requires that $\left[R_{xy}^{(1)}\right]'$ be unchanged by the transformation, i.e., that

$$\left[R_{xy}^{(1)}\right]' = R_{xy}^{(1)}. \tag{3.40}$$

The only possible conclusion is that

$$R_{xy}^{(1)} = 0. \tag{3.41}$$

The same analysis applied to the other axis combinations gives the general first-order relations $R_{\alpha\beta}^{(1)} = 0$, for all $\alpha \neq \beta$. This means that an electric field polarized along a particular axis cannot induce a polarization along a different axis in isotropic media. Moreover, symmetry under the exchanges [Eq. (3.33) - (3.35)] implies that $R_{\alpha\alpha} = R_{\beta\beta}$ for all α and β. Thus the first order response tensor for a isotropic system is specified by a single scalar function

$$R^{(1)} = R_{xx}^{(1)} = R_{yy}^{(1)} = R_{zz}^{(1)}. \tag{3.42}$$

Symmetry arguments for higher-order response tensor elements follow much the same process, but we will defer any detailed discussion until we consider specific experimental scenarios. One result of strikingly broad applicability, however, is worth noting here: since any *even*-order response tensor element possesses an *odd* number of tensor indices, it must always undergo a sign change under the inversion transformation $(x, y, z) \to (-x, -y, -z)$.

But since Von Neumann's principle implies that the tensor element cannot change under inversion, we see that *all even-order response tensor elements vanish for isotropic media*.

In non-isotropic media, such as crystalline solids or liquids with long-range order, the situation can be considerably more complex, especially when considering nonlinear response. In this case, we must consider the specific symmetries of the material and derive relations among the different components of the response tensor. For crystalline solids the non-zero elements of the response tensor are determined by which of 230 three-dimensional space groups they belong to.

3.2   Linear Response

Even with the help of our response theory expressions for the polarization, solving Maxwell's equations in matter is often quite a difficult task. Fortunately, it turns out that the optical response of most materials is dominated by the linear response tensor $R^{(1)}(\tau)$. In this case, solutions to Maxwell's equations are remarkably simple and physically intuitive.

3.2.1   Solving Maxwell's Equations

Linear spectroscopy in dielectric materials is governed by the four equations [Eqs. (3.1a) - (3.1d)], along with the linear response relation

$$P_\alpha^{(1)}(t) = \sum_\beta \int_{-\infty}^\infty d\tau R_{\alpha\beta}^{(1)}(\tau) E_\beta(t - \tau), \tag{3.43}$$

the particular case of Eq. (3.20) for $n = 1$. In this section we will restrict our attention to the case of isotropic dielectrics, so that the response tensor $R^{(1)}$ is diagonal and completely specified by a scalar quantity $R^{(1)}(\tau)$. (Note also that, by symmetry, the zero-field polarization $P^{(0)}$ must vanish for such materials.) In this case, Eq. (3.43) can be written

$$P^{(1)}(t) = \int_{-\infty}^\infty d\tau R^{(1)}(\tau) E(t - \tau), \tag{3.44}$$

implying at once that the polarization in the sample is parallel to the polarization of the electric field.

Solving Maxwell's equations with this complicated function plugged into them may not look like an easy task. But the solution becomes much clearer if we transform to the Fourier domain in the time coordinate. Let us introduce the partially-transformed field

$$\check{E}(x, \omega) \equiv \int_{-\infty}^\infty dt e^{i\omega t} E(x, t), \tag{3.45}$$

along with the corresponding polarization density $\check{\boldsymbol{P}}(\boldsymbol{x}, \omega)$. Note then what happens when we perform a partial Fourier-transform over Eq. (3.44) and exchange the order of integration:

$$\check{\boldsymbol{P}}^{(1)}(\omega) = \int dt e^{i\omega t} \boldsymbol{P}^{(1)}(t) = \int dt e^{i\omega t} \int d\tau R^{(1)}(\tau) \boldsymbol{E}(t - \tau) \tag{3.46}$$

$$= \int d\tau R^{(1)}(\tau) \int dt e^{i\omega t} \boldsymbol{E}(t - \tau). \tag{3.47}$$

Making the change of variables $t' = t - \tau$ produces

$$\check{\boldsymbol{P}}^{(1)}(\omega) = \check{\boldsymbol{E}}(\omega) \int d\tau R^{(1)}(\tau) e^{i\omega\tau} \tag{3.48}$$

$$\equiv \chi(\omega) \check{\boldsymbol{E}}(\omega), \tag{3.49}$$

where χ (defined in the last line) is simply the Fourier transform of the linear response function and is typically referred to as the linear susceptibility. Thus in the Fourier domain, *the linear polarization density is directly proportional to the electric field*.

   This observation suggests that we perform the same partial Fourier transformation on Maxwell's equations [Eqs. (3.1a) - (3.1d)]. Together with Eq. (3.48), this produces a set of homogeneous different equations

$$(1 + 4\pi\chi) \nabla \cdot \check{\boldsymbol{E}} = 0 \tag{3.50a}$$

$$\nabla \cdot \check{\boldsymbol{B}} = 0 \tag{3.50b}$$

$$\nabla \times \check{\boldsymbol{E}} - \frac{i\omega}{c} \check{\boldsymbol{B}} = 0 \tag{3.50c}$$

$$\nabla \times \check{\boldsymbol{B}} + \frac{i\omega}{c} (1 + 4\pi\chi) \check{\boldsymbol{E}} = 0 \tag{3.50d}$$

that resemble quite strongly the vacuum equations [Eq. (2.2a) - (2.2d)]. In fact, the only distinction is the addition of the scaling factor $1 + 4\pi\chi$ in Eqs. (3.50a) and (3.50d)]. Since $\chi(\omega)$ always occurs in this combination in linear optics, one often works instead with the *electric permittivity*

$$\varepsilon(\omega) = 1 + 4\pi\chi(\omega) \tag{3.51}$$

to simplify the form of the equations.

   Following essentially the same procedure we used to solve the vacuum-field equations, we take the curl of Eq. (3.50c), use the identity [Eq. (2.61)] to simplify the double cross product, and use Eq. (3.50d) to eliminate the magnetic field and Eq. (3.50a) to eliminate the divergence of the field. The result is a homogeneous equation

$$\nabla^2 \check{\boldsymbol{E}} + \frac{\omega^2}{c^2} \varepsilon \check{\boldsymbol{E}} = 0 \tag{3.52}$$

that produces solutions of the form

$$\check{E}(x, \omega) = \tilde{A}(\omega)e^{i\frac{\omega}{c}\sqrt{\varepsilon}\hat{s}\cdot x} \tag{3.53}$$

where $\hat{s}$ is any real unit vector. In the time domain, this solution resembles a propagating wave

$$E(x, t) = \int d\omega \tilde{A}(\omega)e^{-i\frac{\omega}{c}\left(ct - \sqrt{\varepsilon}\hat{s}\cdot x\right)} \tag{3.54}$$

but with an amplitude and phase that change with x due to the permittivity $\sqrt{\varepsilon}$. The complete solution for a given situation will consist of a linear combination of such solutions with different $\hat{s}$ vectors, depending on the boundary conditions of the problem.

3.2.2 Absorption Spectroscopy

As a concrete example, consider an ideal beam of the form [Eq. (2.26)] propagating along the z axis ($\hat{s} = \hat{z}$ that at $z = 0$ encounters a semi-infinite sample lying in the xy plane with a finite length ℓ along the z axis but infinite dimensions in x and y. The boundary conditions of the problem require that the field in the sample have the same value as the vacuum fields at $z = 0$ and $z = \ell$, leading to a solution of the form

$$\check{E}(x, \omega) = \tilde{A}(\omega) \cdot \begin{cases} e^{i\frac{\omega}{c}z}, & z < 0 \\ e^{i\frac{\omega}{c}\sqrt{\varepsilon(\omega)}z}, & 0 \le z \le \ell \\ e^{i\frac{\omega}{c}\left(\sqrt{\varepsilon(\omega)}\ell + z\right)}, & z > \ell \end{cases} \tag{3.55}$$

Relative to the vacuum field, the sample thus imparts both a phase (depending on the real part of $\sqrt{\varepsilon(\omega)}$) and a decrease in amplitude (depending on the imaginary part).

Experimentally, the attenuation of beam intensity with distance is monitored in *absorption* spectroscopy. The frequency-resolved intensity $I(\omega)$ of a beam is measured after passage through the sample of interest and is compared to the intensity $I_o(\omega)$ measured in the absence of the sample. The ratio

$$T(\omega) = \frac{I(\omega)}{I_o(\omega)} \tag{3.56}$$

is called the *transmittance* and, for the scenario of Eq. (3.55) takes the form

$$T(\omega) = \frac{\left\|\tilde{A}(\omega)\right\|^2 e^{-\frac{2\omega}{c}\mathrm{Im}\sqrt{\varepsilon(\omega)}\ell}}{\left\|\tilde{A}(\omega)\right\|^2} = e^{-\frac{2\omega}{c}\mathrm{Im}\sqrt{\varepsilon(\omega)}\ell} \tag{3.57}$$

For convenience the exponential is often eliminated by reporting instead a logarithmic quantity, the *absorbance*

$$A(\omega) = -\log T(\omega) = \frac{2\omega\ell}{c\ln 10}\mathrm{Im}\sqrt{\varepsilon(\omega)}. \tag{3.58}$$

Since it is the imaginary part of $\sqrt{\varepsilon}$ that is measured in such experiments, it is often given its own symbol as the *extinction coefficient*

$$\kappa(\omega) \equiv \mathrm{Im}\sqrt{\varepsilon(\omega)}. \tag{3.59}$$

The corresponding quantity

$$n(\omega) \equiv \mathrm{Re}\sqrt{\varepsilon(\omega)} \tag{3.60}$$

is termed the *index of refraction* and determines the phase shift acquired by each frequency component of a beam as it propagates through a linear medium. For many systems of experimental interest, where $\mathrm{Im}\chi(\omega) \ll 1$, the two quantities may be expressed approximately as

$$n(\omega) \approx \sqrt{1 + 4\pi\mathrm{Re}\chi} \tag{3.61}$$

$$\kappa(\omega) \approx \frac{2\pi\mathrm{Im}\chi}{n(\omega)}. \tag{3.62}$$

In this case, the absorbance can be expressed simply as a function of the linear susceptibility via

$$A(\omega) = \frac{4\pi\omega\ell}{cn(\omega)\ln 10}\mathrm{Im}\chi(\omega). \tag{3.63}$$

What's really going on?

The equations of electrodynamics have an uncanny knack for masking the physics that underlies what's really going on. On the one hand, this is fortunate –we needn't worry about too much to calculate things like absorption coefficients. On the other hand, we tend to forget about what's actually happening when light and matter interact.

Contained implicitly with an equation as simple as (3.63) is the fact that as the light passes through the material, it accelerates the electrons bound to the molecules that make up said material. These electrons are displaced from their equilibrium positions, generating a dipole moment, so they too begin to oscillate at the frequency of the driving light. The oscillating dipoles radiate their own waves, which in interferes with the drive and eventually ends up on our detector.

You may be wondering how we can measure absorption if each dipole is radiating. Shouldn't we see some constant radiation pattern? It turns out that the whole story is contained in the *phase* of the radiated waves. If we had treated this from the microscopic perspective of a driven dipole, we would see that the waves radiated in the propagation direction of the driving field are perfectly *out of phase* with the driving field itself. Therefore, the intensity we measure in the forward direction is smaller –this is what we call absorption.

Where does the energy go? Well a dipole doesn't only radiate in the direction of the driving field, so energy from the mode of the driving field is distributed into other modes of the field. In other words, we measure light intensity in other directions –this

is what we call fluorescence. Of course, fluorescence doesn't always occur. In our example above, it doesn't occur due to the artificial infinite slab we considered. In real systems, it may not occur of the energy put into the system is rapidly converted to low-frequency molecular motions, or heat.

3.3 Nonlinear Response and N-Wave Mixing

The linear response assumption turns out to be remarkably accurate for most materials under moderate field intensities. As the field intensity increases, however, any real material will eventually show signs of *nonlinear response*, polarization effects that are proportional to higher orders in the field.[2] In contrast to the linear response regime, it is difficult to obtain exact solutions to Maxwell's equations under almost any circumstances involving nonlinear response.

We can, however, obtain approximate solutions that adequately describe most experimental measurements. To begin, let us separate the linear and nonlinear contributions to the polarization via the definition

$$\boldsymbol{P}^{(\mathrm{NL})}(\boldsymbol{x},t) = \boldsymbol{P}(\boldsymbol{x},t) - \boldsymbol{P}^{(1)}(\boldsymbol{x},t), \tag{3.64}$$

where $\boldsymbol{P}^{(1)}$ is defined by Eq. (3.20). Since we can solve Maxwell's equations exactly for the linear polarization (alone), this will serve as a convenient starting point for approximate treatments. Maxwell's equations (for homogeneous dielectric materials) can now be written

$$\nabla \cdot \left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)}\right) = -4\pi \boldsymbol{P}^{(\mathrm{NL})} \tag{3.65a}$$

$$\nabla \cdot \boldsymbol{B} = 0 \tag{3.65b}$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0 \tag{3.65c}$$

$$\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial}{\partial t}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)}\right) = \frac{4\pi}{c}\frac{\partial \boldsymbol{P}^{(\mathrm{NL})}}{\partial t}. \tag{3.65d}$$

Following now our usual prescription (take the curl of Eq. (3.65c), use identity [Eq. (2.61)] to simplify the double cross-product and Eq. (3.65d) to eliminate the magnetic field), we obtain an equation

$$\nabla\left(\nabla \cdot \boldsymbol{E}\right) - \nabla^2 \boldsymbol{E} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)}\right) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{P}^{(\mathrm{NL})} \tag{3.66}$$

for the electric field alone in terms of the total polarization.

---

[2]To get a sense of scale, the most intense sunlight on a hot summer afternoon falls about 8 orders of magnitude short in field strength of eliciting a nonlinear response in most media.

3.3.1   The Longitudinal and Transverse Fields

This equation resembles the wave equations we have studied already, but is complicated by the apperance of the $\nabla \cdot \boldsymbol{E}$ term which, for nonlinear media, is not necessarily zero. Its behavior is much easier to analyze in Fourier space, taking the form

$$-\boldsymbol{k}\left(\boldsymbol{k}\cdot\tilde{\boldsymbol{E}}\right) + k^2\tilde{\boldsymbol{E}} - \frac{\omega^2}{c^2}\left(\tilde{\boldsymbol{E}} + 4\pi\tilde{\boldsymbol{P}}^{(1)}\right) = \frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}^{(\mathrm{NL})}. \tag{3.67}$$

Observe now, that in $\boldsymbol{k}$-space, the total field $\tilde{\boldsymbol{E}}$ can be expressed as the sum

$$\tilde{\boldsymbol{E}} = \tilde{\boldsymbol{E}}_{\parallel} + \tilde{\boldsymbol{E}}_{\perp} \tag{3.68}$$

of two orthogonal components

$$\tilde{\boldsymbol{E}}_{\parallel}(\boldsymbol{k}, \omega) = \boldsymbol{k}\frac{\boldsymbol{k}\cdot\tilde{\boldsymbol{E}}(\boldsymbol{k}, \omega)}{k^2} \tag{3.69}$$

$$\tilde{\boldsymbol{E}}_{\perp}(\boldsymbol{k}, \omega) = -\frac{\boldsymbol{k}\times\left(\boldsymbol{k}\times\tilde{\boldsymbol{E}}(\boldsymbol{k}, \omega)\right)}{k^2} \tag{3.70}$$

termed the *longitudinal field* ($\tilde{\boldsymbol{E}}_{\parallel}$) and the *transverse field* ($\tilde{\boldsymbol{E}}_{\perp}$). (Note that Eq. (3.68) follows immediately from the definitions [Eqs. (3.69) and (3.70)] using equality [Eq. (2.100)].) At each point $\boldsymbol{k}$ in Fourier-space, the longitudinal field corresponds simply to the projection along $\boldsymbol{k}$, while $\tilde{\boldsymbol{E}}_{\perp}$ is the orthogonal complement. Inserting Eq. (3.68) into Eq. (3.67) and defining analogous transverse and longitudinal components for the polarization terms, we obtain two separate equations

$$-\tilde{\boldsymbol{E}}_{\parallel} + 4\pi\tilde{\boldsymbol{P}}_{\parallel}^{(1)} = -4\pi\tilde{\boldsymbol{P}}_{\parallel}^{(\mathrm{NL})} \tag{3.71}$$

$$\left(k^2 - \frac{\omega^2}{c^2}\right)\tilde{\boldsymbol{E}}_{\perp} + \frac{\omega^2}{c^2}4\pi\tilde{\boldsymbol{P}}_{\perp}^{(1)} = \frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}_{\perp}^{(\mathrm{NL})} \tag{3.72}$$

characterizing the longitudinal and transverse fields.

   Our results so far are exact, and one might almost suspect that we can solve these equations directly. The longitudinal equation is particularly straightforward since all factors of k and ω have disappeared from the final expression, meaning that the equation is algebraic in both Fourier space *and* real space: the longitudinal nonlinear polarization is simply proportional to the electric field plus the linear polarization. The transverse equation is more complicated but strongly resembles the wave equations we've already encountered.

   There is, however, a fundamental difficulty that prevents us from proceeding with exact results: The polarization terms (both linear and nonlinear) in each equation depend on the *total electric field* so that (1) the longitudinal and transverse equations may be coupled via any dependence of $\tilde{\boldsymbol{P}}_{\perp}$ on $\boldsymbol{E}_{\parallel}$ or vice versa, and (2) the transverse equation differs from a true wave equation in that *the source term is itself dependent on the field*. In the next section, we introduce an approximation that, for the particular case of isotropic media, eliminates both difficulties.

3.3.2 The Rare Medium Approximation in Isotropic Media

Although all real materials exhibit nonlinear response at sufficiently high field intensities, the optical response of many systems is sufficiently weak that the total electric field in the sample differs only slightly from the "applied field" – i.e., the electric field that would be present (under the given experimental boundary conditions) *in the absence of the sample*. The *rare medium approximation* takes advantage of this fact to simplify Eqs. (3.71) and (3.72). For the particular case of isotropic media, this simplification completely decouples the two field components.

To this end, let us decompose the total field in the sample as

$$E = E_{\text{ext}} + E^{(1)} + E^{(\text{NL})}, \tag{3.73}$$

where E_{ext} is the external field (the field that would solve Maxwell's equations in the absence of the sample), $E^{(1)}$ is the correction necessary so that the combined field $E_{\text{ext}} + E^{(1)}$ solves Maxwell's equations under the linear response approximation for the material, and $E^{(\text{NL})}$ is whatever correction remains necessary so that $E_{\text{ext}} + E^{(1)} + E^{(\text{NL})}$ solves the complete set of nonlinear Maxwell's equations.

For optically rare materials (i.e., those with weak overall optical response), the corrections $E^{(1)}$ and particularly $E^{(\text{NL})}$ are weak, by definition. This suggests that we can obtain accurate approximations to the true nonlinear response by allowing both $P^{(\text{NL})}$ to be determined solely by the linear field $E_{\text{ext}} + E^{(1)}$, rather than by the total field. In functional notation, this means

$$P^{(\text{NL})}[E] \approx P^{(\text{NL})}\left[E_{\text{ext}} + E^{(1)}\right], \tag{3.74}$$

where the functional form of $P^{(\text{NL})}[E]$ is determined by the nonlinear response expansion of Eqs. (3.17) and (3.20).

For isotropic materials, this approximation is, in some sense, the definitive solution to our difficulties. The linear field $E_{\text{ext}} + E^{(1)}$ and the linear polarization $P^{(1)} = 4\pi\chi^{(1)}(\omega)\left(E_{\text{ext}} + E^{(1)}\right)$ are, in this case, simply the solutions to Maxwell's equations studied in Section (3.2), which is entirely transverse (i.e., the longitudinal component vanishes). Equation (3.71) then becomes simply

$$\tilde{E}_{\parallel}^{(\text{NL})} = -4\pi\tilde{P}_{\parallel}^{(\text{NL})}\left[\tilde{E}_{\text{ext}} + \tilde{E}^{(1)}\right]. \tag{3.75}$$

This longitudinal field is purely local: due to the absence of derivatives in either time or space, the longitudinal field vanishes outside the sample (i.e. the longitudinal polarization does not radiate) and is thus of little interest experimentally. Moreover, under the rare medium approximations $\tilde{P}_{\perp}$ is independent of $\tilde{E}_{\parallel}$, so that in practice the longitudinal field can, for most purposes, be neglected entirely.

The transverse field exhibits much more interesting behavior. Under the rare medium approximation in isotropic media, Eq. (3.72) becomes[3]

$$
\left(k^2 - \frac{\omega^2}{c^2}\varepsilon(\omega)\right)\left(\tilde{E}_{\text{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right) + \left(k^2 - \frac{\omega^2}{c^2}\varepsilon(\omega)\right)\tilde{\boldsymbol{E}}_\perp^{(\text{NL})}
$$
$$
= \frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}_\perp^{(\text{NL})}\left[\tilde{E}_{\text{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right]. \tag{3.76}
$$

But by definition of $\tilde{\boldsymbol{E}}^{(1)}$, the first term here is identically zero, so that

$$
\left(k^2 - \frac{\omega^2}{c^2}\varepsilon(\omega)\right)\tilde{\boldsymbol{E}}_\perp^{(\text{NL})} = \frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}_\perp^{(\text{NL})}\left[\tilde{E}_{\text{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right]. \tag{3.77}
$$

Critically – and in contrast to Eq. (3.75) for the longitudinal field – this equation is capable of supporting nonlinear components of the electric field *outside the sample*. In fact, outside the sample the right hand side vanishes and $\varepsilon(\omega) = 1$, so that the equation reduces simply to the homogeneous wave equation. Physically, this means that nonlinear transverse fields generated *inside* the sample can radiate *out of* the sample, propagating outward as the electromagnetic waves studied in Section 2.1.

3.3.3   N-Wave Mixing

In Fourier space, Eq. (3.77) is solved trivially as

$$
\tilde{\boldsymbol{E}}^{(\text{NL})} = 4\pi\frac{\tilde{\boldsymbol{P}}^{(\text{NL})}\left[\tilde{\boldsymbol{E}}_{\text{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right]}{\frac{c^2k^2}{\omega^2} - \varepsilon(\omega)} \tag{3.78}
$$

in terms of the nonlinear polarization density. Note that here, and throughout the text, we drop the subscript $\perp$ for the transverse field since the longitudinal field is not usually experimentally measurable and (for optically rare, isotropic media) does not mix with the transverse field.

Despite this simple Fourier representation, transforming back to real space is rather involved, so we will defer any discussion of explicit real-space solutions until we need them to describe specific experiments. Without difficulty, however, a great deal of physical insight can be obtained from Eq. (3.78) by examining the conditions under which the nonlinear field can be nonzero. First, however, we must provide an explicit form for $\tilde{\boldsymbol{P}}^{(\text{NL})}$ in Fourier space. Appling the definition [Eq. (2.15)] of the Fourier transform to Eq. (3.20) gives directly

$$
\tilde{P}_\alpha^{(n)}\left[\tilde{\boldsymbol{E}}^{(\text{exc})}\right] = \sum_{\alpha_1,\dots,\alpha_n}\int d\tau_n\dots\int d\tau_1 R_{\alpha_1\dots\alpha_n\alpha}^{(n)}(\tau_1,\dots,\tau_n) \tag{3.79}
$$
$$
\times \int_V d\boldsymbol{x}\int dt\, e^{i(\omega t - \boldsymbol{k}\cdot\boldsymbol{x})}E_{\alpha_1}^{(\text{exc})}(\boldsymbol{x}, t - \tau_1 - \dots - \tau_n)\dots E_{\alpha_n}^{(\text{exc})}(\boldsymbol{x}, t - \tau_n),
$$

---

[3]Note that we have dropped the subscripts $\perp$ on $\tilde{E}_{\text{ext}}$ and $\tilde{\boldsymbol{E}}^{(1)}$ since both are completely transverse in isotropic media.

where

$$\tilde{\boldsymbol{E}}^{(\text{exc})} = \tilde{\boldsymbol{E}}_{(\text{ext})} + \tilde{\boldsymbol{E}}^{(1)} \tag{3.80}$$

is the "excitation" field that (under the rare medium approximation) induces the nonlinear polarization, and where the integration over $\boldsymbol{x}$ is limited to the sample volume V since the polarization vanishes outside of the sample.

Casting the excitation fields in terms of their transforms

$$E_{\alpha_i}^{(\text{exc})}(\boldsymbol{x}, t - \tau_i - \dots - \tau_n) = \frac{1}{(2\pi)^4} \int d\omega_i \int d\boldsymbol{k}_i \tilde{E}_{\alpha_i}^{(\text{exc})}(\boldsymbol{k}_i, \omega_i) \tag{3.81}$$
$$\times\, e^{-\mathrm{i}\omega_i(t-\tau_i-\dots-\tau_n)} e^{\mathrm{i}\boldsymbol{k}_i\cdot\boldsymbol{x}},$$

reordering the integrals, and combining exponents, this becomes

$$\tilde{P}_{\alpha}^{(n)}(\boldsymbol{k}, \omega) = \frac{1}{(2\pi)^{4n}} \sum_{\alpha_1,\dots,\alpha_n} \int d\omega_1 \dots \int d\omega_n \int d\boldsymbol{k}_1 \dots \int d\boldsymbol{k}_n \tag{3.82}$$
$$\times\, \tilde{E}_{\alpha_1}^{(\text{exc})}(\boldsymbol{k}_1, \omega_1) \dots \tilde{E}_{\alpha_n}^{(\text{exc})}(\boldsymbol{k}_n, \omega_n)$$
$$\times \int d\tau_n \dots \int d\tau_1 \, R_{\alpha_1\dots\alpha_n\alpha}^{(n)}(\tau_1, \dots, \tau_n) e^{\mathrm{i}\omega_1\tau_1} e^{\mathrm{i}(\omega_1+\omega_2)\tau_2} \dots e^{\mathrm{i}(\omega_1+\dots+\omega_n)\tau_n}$$
$$\times \int_V d\boldsymbol{x} \int dt \, e^{\mathrm{i}(\boldsymbol{k}_1+\dots+\boldsymbol{k}_n-\boldsymbol{k})\cdot\boldsymbol{x}} e^{-\mathrm{i}(\omega_1+\dots+\omega_n-\omega)t}.$$

The second-to-last line here is exactly the Fourier transform of the response function, evaluated at the successive frequencies ω_1, $\omega_1 + \omega_2$, etc. The final integral dt is exactly the Dirac delta function $2\pi\delta(\omega_1 + \dots + \omega_n - \omega)$. The integral $d\boldsymbol{x}$ is *almost* a delta function in $\boldsymbol{k}$ but differs due to the finite volume V of the sample. Although such finite-size effects can be important for very small samples (e.g., the nonlinear properties of a single nanoparticle), for macroscopic samples and optical wavelengths, it is usually an excellent approximation to extend the integration limits to cover all space. In this case, we obtain

$$\tilde{P}_{\alpha}^{(n)}(\boldsymbol{k}, \omega) \approx \frac{1}{(2\pi)^{4(n-1)}} \sum_{\alpha_1,\dots,\alpha_n} \int d\omega_1 \dots \int d\omega_n \int d\boldsymbol{k}_1 \dots \int d\boldsymbol{k}_n \tag{3.83}$$
$$\times\, \delta(\omega_1 + \dots + \omega_n - \omega)\, \delta(\boldsymbol{k}_1 + \dots + \boldsymbol{k}_n - \boldsymbol{k})$$
$$\times\, \tilde{R}_{\alpha_1\dots\alpha_n\alpha}^{(n)}(\omega_1, \dots, \omega_1 + \dots + \omega_n)$$
$$\times\, \tilde{E}_{\alpha_1}^{(\text{exc})}(\boldsymbol{k}_1, \omega_1) \dots \tilde{E}_{\alpha_n}^{(\text{exc})}(\boldsymbol{k}_n, \omega_n).$$

Because the nth-order polarization density is determined by a product of excitation fields sampled at n different points in Fourier space, and because this induced polarization gives rise, under Eq. (3.78) to propagating waves with a new wavevector $\boldsymbol{k}$ and frequency ω, experiments that measure the nth-order field are often term $(n+1)$-*wave mixing* experiments.[4]

---

[4]The "n" refers to the excitation waves corresponding to Fourier points $(\boldsymbol{k}_i, \omega_i)$, while the "+1" refers to the generated signal.

3.3.4   Signal Frequencies and Wavevectors

From this expression, we can concretely analyze the conditions necessary to observe non-linear signals. The most apparent restriction is that the pair of delta functions in ω and $\boldsymbol{k}$ enforce two strict "sum conditions" for the emitted signal:

$$\omega = \omega_1 + ... + \omega_n \tag{3.84}$$

$$\boldsymbol{k} = \boldsymbol{k}_1 + ... + \boldsymbol{k}_n, \tag{3.85}$$

where ω_i and $\boldsymbol{k}_i$ are the frequencies and wavevectors at which the field components $\tilde{E}_{\alpha_i}$ are sampled. If the excitation fields $\tilde{E}_{\alpha_i}$ are strongly peaked in $\boldsymbol{k}$ and/or ω, the signal frequencies ω and $\boldsymbol{k}$ are strongly constrained by Eqs. (3.84) and (3.85). Note, however, that the frequencies ω_i and wavevectors $\boldsymbol{k}_i$ may have either positive or negative signs: due to the symmetry constraint [Eq. (2.19)] on the electric field, any field $\tilde{E}(\boldsymbol{k}, \omega)$ with a strong peak near $(\boldsymbol{k}_i, \omega_i)$ must also exhibit a strong peak near $(-\boldsymbol{k}_i, -\omega_i)$.

3.3.5   Phase Matching

Although perhaps less obvious, the restrictions [Eqs. (3.84) and (3.85)] imply an additional restriction on nonlinear signals. Inserting Eq. (3.83) into Eq. (3.78), bringing the prefactor $\left(\frac{c^2 k^2}{\omega^2} - \varepsilon(\omega)\right)^{-1}$ inside the integral, and using the summation conditions [Eqs. (3.84) and (3.85)], we obtain

$$\tilde{E}^{(\text{NL})}(\boldsymbol{k}, \omega) = \frac{4\pi}{(2\pi)^{4(n-1)}} \sum_{\alpha_1,...,\alpha_n} \int d\omega_1 ... \int d\omega_n \int d\boldsymbol{k}_1 ... \int d\boldsymbol{k}_n \tag{3.86}$$

$$\times \, \delta\left(\omega_1 + ... + \omega_n - \omega\right) \delta\left(\boldsymbol{k}_1 + ... + \boldsymbol{k}_n - \boldsymbol{k}\right)$$

$$\times \, \tilde{R}^{(n)}_{\alpha_1...\alpha_n\alpha}(\omega_1, ..., \omega_1 + ... + \omega_n)$$

$$\times \, \frac{\tilde{E}^{(\text{exc})}_{\alpha_1}(\boldsymbol{k}_1, \omega_1)...\tilde{E}^{(\text{exc})}_{\alpha_n}(\boldsymbol{k}_n, \omega_n)}{\frac{c^2 \|\boldsymbol{k}_1 + ... + \boldsymbol{k}_n\|^2}{(\omega_1 + ...\omega_n)^2} - \varepsilon(\omega_1 + ...\omega_n)}.$$

When the denominator in this expression nears zero, the nonlinear field will be strongly enhanced, leading to the *phase-matching condition*[5]

$$\frac{c^2 \|\boldsymbol{k}_1 + ... + \boldsymbol{k}_n\|^2}{(\omega_1 + ...\omega_n)^2} \approx \varepsilon(\omega_1 + ...\omega_n). \tag{3.87}$$

Although the magnitude of the polarization itself is unaffected by this condition, induced polarizations that do *not* satisfy Eq. (3.87) will generally not radiate.

---

[5]Note that phase-matching can never be *exactly* satisfied since the left-hand side of Eq. (3.87) is strictly real, while for real materials the right-hand side always possesses a non-zero imaginary part, representing absorption of the field. This ensures that the field, under Eq. (3.78), is always finite.

In the particular case that the excitation field has a well-defined propagation axis $\hat{s}_o$, the phase-matching condition can be stated more concretely in terms of the refractive index. As the linear solution to Maxwell's equations, the excitation field $\tilde{E}^{(\mathrm{exc})}$ satisfies approximately the dispersion relation

$$\|\boldsymbol{k}\| \approx n(\omega)\frac{\omega}{c}. \tag{3.88}$$

If the propagation axis is well-defined, we must then have

$$\boldsymbol{k}_i = n(\omega_i)\frac{\omega_i}{c}\hat{s}_o \tag{3.89}$$

for each $1 \le i \le n$. The phase-matching condition [Eq. (3.87)] then becomes

$$n(\omega_1)\omega_1 + ... + n(\omega_n)\omega_n \approx n(\omega_1 + ...\omega_n)(\omega_1 + ...\omega_n). \tag{3.90}$$

If the index of refraction $n(\omega)$ is independent of frequency over the interval of interest, this condition is automatically satisfied. This will often be the case when the signs of the individual frequencies ω_i alternate, e.g., $\omega_1 \approx -\omega_2 \approx \omega_3, ...$ For example, the four-wave mixing experiment known as pump-probe spectroscopy is automatically phase-matched. If the individual frequencies ω_i all have the same sign, however, phase-matching will generally not be satisfied, leading to a strong suppression of nonlinear signals. For example, third-harmonic generation is a third-order experiment for which $\omega_1 \approx \omega_2 \approx \omega_3$, so that the signal frequency is roughly three times the frequency of the excitation field. Since for most systems $n(\omega) \ne n(3\omega)$, such processes are strongly suppressed in isotropic media, and third-harmonic generation is usually restricted to anisotripic materials where phase-matching can be accomplished by taking advantage of the fact that different crystal axes may exhibit different refractive indices.

What's in a phase?

It is often stated that phase matching (or equivalently, wavevector matching as in Eq. (3.85)) is a consequence of conservation of momentum. *This is a incorrect.* All light matter interactions conserve momentum; phase matching is special.

The physics that underlies phase matching is implied in the name –some phases need to be matched to each other to produce nonlinear signal. To see which phases, consider that the nonlinear polarization is a running wave with frequency $\omega_1 + \omega_2 + \ldots$ and wavevector $\boldsymbol{k}_1 + \boldsymbol{k}_2 + \ldots$ (see Eq. (3.20)) which are determined by the excitation field. This means that each point in the sample is radiating some contribution to $\boldsymbol{E}^{(\mathrm{NL})}$, but with an amplitude and phase determined by the excitation field. If each point of radiation doesn't add *coherently* with every other, destructive interference occurs and $\boldsymbol{E}^{(\mathrm{NL})}$ outside the sample is tiny.

In other words, $\boldsymbol{E}^{(\mathrm{NL})}$ is a running wave in its own right, and it needs to run at the same rate as $\boldsymbol{P}^{(\mathrm{NL})}$ in order for a macroscopic electric field to be generated. If $\boldsymbol{E}^{(\mathrm{NL})}$ and $\boldsymbol{P}^{(\mathrm{NL})}$ are at the same frequency, this is trivial. If they are different (as in third harmonic generation) then the only way to ensure that $\boldsymbol{E}^{(\mathrm{NL})}$ and $\boldsymbol{P}^{(\mathrm{NL})}$ run at the same

rate is if Eq. (3.90) is satisfied.

This is evident in cases where all wavevectors are not parallel as well. Consider a sum frequency generation experiment where the two driving lasers impinge on the system at $90°$ relative to each other. The resulting polarization runs along the line that bisects the angle between the two wavevectors, and indeed, $\boldsymbol{E}^{(\text{NL})}$ is radiated along this line.

This may all seem like splitting hairs –after all, phase matching does conserve momentum. The important point here is that there are also *incoherent* nonlinear processes, which do not generate a macroscopic $\boldsymbol{E}^{(\text{NL})}$, that still occur, though these processes generate signals bearing no phase relation to the excitation field (such as two-photon absorption followed by fluorescence).

3.3.6   Response Function Resonances

Finally, and perhaps of most interest to the spectroscopist, the nonlinear signal depends strongly on *resonance* between the excitation field and the nonlinear response tensor $\boldsymbol{R}^{(n)}$. The response tensors for most materials are strongly frequency-dependent, exhibiting strong peaks, as we shall see later, at frequencies resonant with the underlying microscopic dynamics of the material. It is exactly this sensitivity of the nonlinear response to microscopic dynamics that gives nonlinear spectroscopy its power as a probe of material systems. The next two chapters examine this relationship in detail, examining the optical properties of a variety of microscopic models for material systems.

3.3.7   The Signal Field

- Neglect Im $\varepsilon(\omega)$

- Take Re $\varepsilon(\omega) \equiv n^2(\omega)$ constant

$$\left(k^2 - \frac{n^2\omega^2}{c^2}\right)\tilde{\boldsymbol{E}}^{(\text{NL})}(\boldsymbol{k},\omega) = \frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}^{(\text{NL})}(\boldsymbol{k},\omega) \tag{3.91}$$

Taking the Fourier transform gives

$$\left(\frac{n^2}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\boldsymbol{E}^{(\text{NL})}(\boldsymbol{x},t) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\tilde{\boldsymbol{P}}^{(\text{NL})}(\boldsymbol{x},t) \tag{3.92}$$

$$\boldsymbol{E}^{(\text{NL})}(\boldsymbol{x},t) = -\frac{4\pi}{c^2}\int d\boldsymbol{x}'\frac{\frac{\partial^2}{\partial t^2}\tilde{\boldsymbol{P}}^{(\text{NL})}(\boldsymbol{x}',t-|\boldsymbol{x}-\boldsymbol{x}'|n/c)}{|\boldsymbol{x}-\boldsymbol{x}'|} \tag{3.93}$$

Assume $\boldsymbol{P}^{(\text{NL})}(t) \propto e^{i\omega(t+\frac{n}{c}z)} + c.c.$

In far-field limit, $|\boldsymbol{x} - \boldsymbol{x}'| \approx z$, so that

$$\boldsymbol{E}^{(\text{NL})}(\boldsymbol{x}, t) = -\frac{4\pi}{c^2} \int \mathrm{d}\boldsymbol{x}' \frac{\frac{\partial^2}{\partial t^2} \tilde{\boldsymbol{P}}^{(\text{NL})}(z, t - zn/c)}{z} \tag{3.94}$$

$$\propto -\frac{4\pi}{c^2} \int \mathrm{d}\boldsymbol{x}' \frac{\frac{\partial^2}{\partial t^2} e^{i\omega t}}{z} \tag{3.95}$$

$$\approx \frac{4\pi}{\omega^2 c^2} \int \mathrm{d}\boldsymbol{x}' \frac{\frac{\partial^2}{\partial t^2} e^{i\omega t}}{z} \tag{3.96}$$

Chapter 4

Quantum Dynamics

4.1 The Postulates of Quantum Mechanics

4.1.1 Introduction

The description of propagating electromagnetic fields developed in the preceding chapters relies on a wholly classical explanation of physics. In contrast, our description of material dynamics will be purely (or almost purely) quantum mechanical. Although we will make no effort here to give a complete description of quantum theory, a cursory introduction is in order.

Perhaps the most fundamental distinction between quantum and classical mechanics is in our philosophical understanding of uncertainty in physical observables. In classical mechanics, the complete physical description of a system is specified by the time-dependent positions x of each particle in the system. If we know $x(t)$ exactly as a function of time, we are able to calculate with arbitrary precision the value of any other mechanical observable (velocity, momentum, energy, etc.) in terms of that trajectory or its derivatives with respect to time. Uncertainty in $x(t)$ may give rise to uncertainty in the derived quantities, but this uncertainty reflects our ignorance of the true value of $x(t)$, not any fundamental ambiguity in the value of the observable.

In quantum theory, in contrast, the complete state of a system is determined not by a coordinate trajectory $x(t)$ but by a wavefunction trajectory $\psi(\alpha, t)$. The *wavefunction* is a purely quantum mechanical creature, depending on time and on some other physical observable α (position, momentum, energy, etc.) for which it acts as a probability amplitude, i.e. $|\psi(\alpha, t)|^2$ gives the probability density for observing the value α in a measurement of the corresponding physical observable at time t. That the wavefunction specifies only a probability amplitude–not the exact value of each physical quantity–reflects a fundamentally different understanding of measurement uncertainty in quantum mechanics as opposed to the classical theory. Whereas classical uncertainty arises from our own ignorance of the system under consideration, quantum uncertainty exists even when our knowledge of the physical state of the system is complete and perfectly precise. Indeed, although a sufficiently sharply-

peaked wavefunction might produce very low uncertainty in the value of α, the postulates of quantum mechanics further demonstrate that wavefunctions with *low* uncertainty in certain parameters give correspondingly *high* uncertainty in other parameters; the inverse relation between uncertainty in the coordinate x and momentum p is perhaps the most famous example.

This cursory introduction raises several important questions. First, how is the wavefunction specified? So far we have simply asserted that it exists, without specifying how we find it or what are its properties. Likewise, we insinuated above that the wavefunction be cast as a function of many different physical parameters, x and p being only two examples. Which parameters are acceptable for this purpose, and how do we pick one? Finally, although we indicated that the wavefunction provides information on many parameters, we described only how it informs us on the probability for the single parameter α on which it depends. How do we obtain information on other observables from the wavefunction?

The remainder of this chapter presents a more extensive description of quantum mechanics by laying out the postulates of the theory (and a few of their implications) in a more definite order.

4.1.2   The First Postulate: Introduction to Hilbert Space

For every physical system, there exists a state vector ψ of unit norm, an element of an infinite-dimensional Hilbert space $\mathcal{H}$, which defines statistically all physical properties of the system. Every unit vector in $\mathcal{H}$ corresponds to a possible physical state of the system, and every physical state of the system corresponds to a specific unit vector in $\mathcal{H}$. [1]

This first postulate simply asserts the existence and physical significance of the state vector, without specifying its form or the manner in which it relates to physical observables. The statement is of no direct value in describing any particular system; its significance, rather, rests in laying the mathematical foundation for quantum mechanics. Whereas the state of a classical system is specified by coordinates x and momenta p, the first postulate states that the state of a quantum system is specified by an element in Hilbert space, a particular flavor of vector space which plays a central role in the mathematics of quantum theory.

Although a detailed examination of the characteristics of Hilbert spaces is beyond the scope of this text, a cursory explanation is in order. For our purposes, a Hilbert space $\mathcal{H}$ consists of a set of elements ϕ (termed *vectors*) which is closed under the addition and (complex) scalar multiplication of its elements and which posesses a well-defined inner product.[2]

---

[1]The statement that each state corresponds to a specific element in $\mathcal{H}$ is rather sloppily stated here. Many equivalent representations are possible for any given state, since an arbitrary phase can be applied to the state vector without changing the physical state *so long as the same phase is applied to every state vector in the Hilbert space*.

[2]This is a list of salient features, not a technical definition. To be more precise, a Hilbert space is a

The mathematical language here, although necessary, should not be intimidating. A "set of elements" here means simply a collection of mathematical objects; examples might be a particular set of numbers, vectors in three-dimensional space, or symmetry operations. Closure under addition means that for any two objects ϕ and ψ in the set $\mathcal{H}$, we know how to add them–that is, we have a rule for what the notation "$\phi + \psi$" means–and that the resulting object $\phi + \psi$ is also an element in $\mathcal{H}$. For example, the set of real numbers is closed under addition since, for any two real numbers a and b, we know what $a + b$ means and since the resulting number $c = a + b$ is also in the set of real numbers. In contrast, the set of real numbers between 0 and 1 is *not* closed under addition since, for example, $\frac{3}{4} + \frac{1}{2} = 1\frac{1}{4}$ is outside the set. Likewise, closure under scalar multiplication means that for any complex scalar α and any vector ϕ in $\mathcal{H}$, the notation $\alpha\phi$ has a well-defined meaning and corresponds to a new vector which is also contained in $\mathcal{H}$. The set of real numbers is *not* closed under complex scalar multiplication since, for example, ia is not a real number; the set of complex numbers, in contrast, is closed under this operation, as is the set of complex, three-element vectors and the set of all matrices with complex elements.

Physically, the properties of addition and scalar multiplication imply that *normalized, linear combinations of state vectors produce new state vectors*. (We will say more about normalization in a moment). In quantum mechanics, it is often useful to decompose a given state vector into a sum of other state vectors about which some particular physical property is known. If we know the physical characteristics of the states $\phi_1, \phi_2, ..., \phi_n$, for example, it may be useful to write another state as a linear combination of these vectors, i.e. $\psi = \alpha_1\phi_1 + \alpha_2\phi_2 + ... + \alpha_n\phi_n$ where $\alpha_1, ..., \alpha_n$ are complex numbers. As we will see later, knowledge of the properties of the states $\phi_1, ..., \phi_n$ then informs us about state ψ. This additivity of state vectors in Hilbert space, where new physical states can correctly be understood as linear combinations of other physical states, plays a fundamental role in both the mathematical and physical characteristics of quantum theory.

In understanding *how* a state vector can (or should) be decomposed into other physical states, the existence of an *inner product* for the elements of $\mathcal{H}$ plays a central role. In a mathematical sense, an inner product is a particular type of mapping which takes any two elements ϕ and ψ of a vector space and assigns to them a specific (complex) scalar, denoted (ϕ, ψ). More precisely, for any three vectors ψ, ϕ, and χ and any complex scalar α, this mapping satisfies four criteria:

1. $(\psi, \phi + \chi) = (\psi, \phi) + (\psi, \chi)$

2. $(\psi, \alpha\phi) = \alpha(\psi, \phi)$

3. $(\psi, \phi) = (\phi, \psi)^*$

4. $(\psi, \psi) \geq 0$, with $(\psi, \psi) = 0$ if and only if ψ is the zero vector (the unique vector in $\mathcal{H}$ for which $\phi + \psi = \phi$ for all vectors ϕ).

complete inner product space, i.e. a vector space which posesses a well-defined inner product and such that every Cauchy sequence of vectors converges (within the metric defined by the inner product) to a vector within the space.

Together, these statements imply a fifth condition, known as the *Cauchy Schwartz inequality*:

$$|(\phi, \psi)| \le \sqrt{(\phi, \phi)(\psi, \psi)}. \tag{4.1}$$

The first two criteria state that the the inner product is *linear* in the addition of state vectors and in scalar multiplication. The third item sets up a complex symmetry for the inner product; up to complex conjugation, the inner product between two vectors does not depend on the order in which they are specified. The complex conjugation property also implies that the inner product of any vector with itself is real since $(\phi, \phi) = (\phi, \phi)^*$ and can be taken as a measure of the "length" of a vector (in a mathematical, not physical, sense); in fact, we define the *vector norm* of a vector ϕ to be the square root of this quantity and denote it $\|\phi\| = \sqrt{(\phi, \phi)}$. We say a vector is *normalized* if $\|\phi\| = 1$. Together with the last inner product criterion, which requires that the inner product of any non-zero vector with itself be positive, these properties imply that the inner product may be taken as a measure of how "similar" two states are to one another; the larger the magnitude of the inner product $|(\phi, \psi)|$–relative to the magnitude of the vector norms $\|\phi\|$ and $\|\psi\|$–the more similar the two states should be considered.[3] States which have inner product zero are said to be *orthogonal*.

Both physically and mathematically, it is often convenient to identify a (possibly infinite) set of vectors $\phi_1, ...\phi_n, ...$ such that *every vector ψ in $\mathcal{H}$ can be written as a linear combination* $\psi = \alpha_1\phi_1 + \alpha_2\phi_2 + ...$ Such a set is called a *basis* for $\mathcal{H}$. It is one of the properties of Hilbert spaces[4] that *a countable basis for $\mathcal{H}$ always exists*[5], and that every basis for $\mathcal{H}$ is countably infinite (i.e. no finite basis exists). Moreover, given a basis for $\mathcal{H}$, it is easy to construct from it an *orthonormal* basis, i.e. one for which every vector has unit norm and is orthogonal to every other vector, $(\phi_i, \phi_j) = \delta_{ij}$.[6]

The practical utility of requiring our basis to be orthonormal becomes clear when we seek to identify the coefficients $\alpha_1, \alpha_2, ...$ in the expansion $\psi = \alpha_1\phi_1 + \alpha_2\phi_2 + ...$ for an aribtrary vector ψ. Observe what happens when we take the inner product of ψ with one of

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[3]Technically, we should be more careful here. Although it is true that two states with a large inner product will exhibit similar physical characteristics, it is not always true that two states with a small inner product are physically very different. In fact, we often encounter states which have identical values of some physical observable (energy, for example) but with an inner product of zero. We say that such states are *degenerate* with respect to this observable. Often, two states may be degenerate with respect to one observable but non-degenerate (i.e. distinguishable) with respect to another.

[4]This is not usually included directly as a defining feature of a Hilbert space. Some authors specify in the definition that a Hilbert space must contain a countably dense set, which is equivalent. Others exclude this property altogether from the definition and distinguish between *separable* and *nonseparable* Hilbert spaces, i.e. those which do and do not posess a countable, dense set and thus a countable basis.

[5]*Countable* means that the elements of the set can be enumerated one at a time; that is, it is possible to establish a "rule" for assigning exactly one positive integer to each vector ($\phi_1, \phi_2, ...$) such that every vector is assigned an integer and no integer is assigned more than once. A finite set of vectors is trivially countable. An infinite set need not be.

[6]Suppose $\phi_1, \phi_2, ...$ is a countable basis for $\mathcal{H}$. Begin by setting $\tilde{\phi}_1 = \frac{\phi_1}{\|\phi_1\|}$ so that $\tilde{\phi}_1$ has unit norm. Next, set $\tilde{\phi}_2 = \frac{\phi_2 - (\tilde{\phi}_1, \phi_2)\tilde{\phi}_1}{\|\phi_2 - (\tilde{\phi}_1, \phi_2)\tilde{\phi}_1\|}$. $\tilde{\phi}_2$ now has unit norm and is orthogonal to $\tilde{\phi}_1$. Proceed for the remaining vectors in

the basis vectors ϕ_i, and use the linearity of the inner product to expand the result:

$$
\begin{aligned}
(\phi_i, \psi) &= (\phi_i, \alpha_1 \phi_1 + \alpha_2 \phi_2 + ...) \\
&= \alpha_1(\phi_i, \phi_1) + \alpha_2(\phi_i, \phi_1) + ... + \alpha_i(\phi_i, \phi_i) + ... \\
&= \alpha_i
\end{aligned}
\tag{4.3}
$$

where in the final equality we have made use of the orthogonality and normalization of the basis vectors $\phi_1, \phi_2, ...$ The result is that the coefficient α_i for basis vector ϕ_i is none other than the inner product (ψ, ϕ_i), i.e. that *for an orthonormal basis $\phi_1, \phi_2, ...,$ every vector ψ in $\mathcal{H}$ may be written in the form*

$$
\psi = \sum_n (\phi_n, \psi)\phi_n.
\tag{4.4}
$$

In this basis, the norm of the vector may be expressed as

$$
\|\psi\|^2 = \sum_n (\phi_n, \psi)^2 = \sum_n \alpha_n^2
\tag{4.5}
$$

where it should be clear that the vector is well-defined only if the sum of the right hand side of the quality converges.

   An important consequence of this property is that we can represent any vector in the Hilbert space as a sequence of numbers $(\alpha_1, \alpha_2, ..., \alpha_n, ...)$ with respect to a given set of orthonormal basis vectors $\phi_1, \phi_2, ...$ This equivalence between the elements of abstract Hilbert space and the more concrete set of numeric vectors $(\alpha_1, \alpha_2, ...)$ is of great practical assistance in navigating the wilds of Hilbert space.

   From a physical perspective, the ability to decompose arbitrary state vectors in this form will have profound consequences in our understanding of physical states in quantum theory. As of yet, of course, we have provided no explanation of how the mathematical structure of Hilbert space and, in particular, the knowledge of the state vector of a system translate into an understanding of physical observables. This relationship will be the focus of the remaining postulates.

The position representation

   The principles of quantum mechanics can be formulated entirely in terms of an abstract Hilbert space $\mathcal{H}$ without specifying any particular form for its elements. For practical purposes, however, it is much more convenient to work in a specific Hilbert space with a concrete mathematical representation for its elements. In the text boxes offset from the statement of the postulates, we thus illustrate some basic workings

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the same manner, i.e.

$$
\tilde{\phi}_n = \frac{\phi_n - (\tilde{\phi}_1, \phi_n)\tilde{\phi}_1 - ... - (\tilde{\phi}_{n-1}, \phi_n)\tilde{\phi}_{n-1}}{\phi_n - (\tilde{\phi}_1, \phi_n)\tilde{\phi}_1 - ... - (\tilde{\phi}_{n-1}, \phi_n)\tilde{\phi}_{n-1}},
\tag{4.2}
$$

discarding any vectors for which the denominator is zero. The set $\{\tilde{\phi}_1, \tilde{\phi}_2, ...\}$ then forms an orthonormal basis for $\mathcal{H}$.

of quantum mechanics in the position representation, one of the most commonly used formulations of quantum mechanics. For simplicity, we will consider only the dynamics of a single particle moving in one dimension.

In the position representation, the dynamics of this system are formulated in the abstract Hilbert space L^2, the space of square-integrable functions of a single variable. The elements of the Hilbert space L^2 consist of all complex-valued functions $f(x)$ such that the integral

$$\int_{-\infty}^{\infty} f^*(x)f(x)dx = \int_{-\infty}^{\infty} |f(x)|^2 dx \tag{4.6}$$

converges to a finite value. It is easy to see that the set of such functions is closed under addition and scalable location since if $f(x)$ and $g(x)$ are square-integrable functions, then $(f + g)(x)$ and $\alpha f(x)$ (for any complex scalar α) are also square-integrable. Moreover, the inner product

$$(f, g) = \int_{-\infty}^{\infty} f^*(x)g(x)dx \tag{4.7}$$

is always well-defined[a] and satisfies the properties of the inner product described in the main text. Many different complete, orthonormal sets are available in L^2. One example is the Hermite functions

$$h_n(x) = \left(\sqrt{\pi}2^n n!\right)^{-\frac{1}{2}} (-1)^n e^{\frac{x^2}{2}} \frac{d^n}{dx^n} e^{-x^2}, \qquad\qquad n = 0, 1, 2, ... \tag{4.9}$$

which we will encounter later in our analysis of the quantum harmonic oscillator.

According to our first postulate, the state of the physical system under consideration (a single particle moving in one dimension) is completely described by some particular function $\psi(x)$ normalized to such that

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1. \tag{4.10}$$

In the position representation, this state vector is commonly referred to as the system *wave function*. Our objective is now to learn how to identify the wave function for a

particular system and how to use it predict the results of physical measurements.

---

^{a}Note that

$$\left(\int_{-\infty}^{\infty} f^*(x)g(x)dx\right)^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f^*(x)g(x)f(y)g^*(y)dxdy$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |f(x)|^2|g(y)|^2dxdy + \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |f(y)|^2|g(x)|^2dxdy$$

$$-\frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |f^*(x)g(x) - f^*(y)g(x)|^2dxdy \leq (f,f) + (g,g). \tag{4.8}$$

4.1.3 The Second Postulate: Hermitian Operators

To every measurable physical quantity A characterizing the state of a system, there corresponds a Hermitian operator $\hat{A}$ operating in $\mathcal{H}$.

Just as the first postulate introduced us to state vectors in Hilbert spaces, the second posulate introduces us to the concept of *linear operators* on Hilbert spaces. Just as the inner product is a rule for assigning a complex number (ϕ, ψ) to each pair of vectors ϕ and ψ in $\mathcal{H}$, an operator $\hat{A}$ is a rule for assigning to each vector ϕ in $\mathcal{H}$ some other vector $\hat{A}\phi$, also in $\mathcal{H}$. An operator is said to be *linear* if it satisfies the two conditions

$$\hat{A}\alpha\phi = \alpha\hat{A}\phi$$
$$\hat{A}(\phi + \psi) = \hat{A}\phi + \hat{A}\psi \tag{4.11}$$

for every complex scalar α and all vectors ϕ and ψ in $\mathcal{H}$. Linear operators play a variety of important roles in quantum mechanics. In addition to defining measurable quantities, they also determine the time evolution of the state vector, and hence the physical state, of quantum systems.

In the last section, we saw that state vectors in a Hilbert space may be associated with numeric vectors $(\alpha_1, \alpha_2, ...)$, where the coefficients α_n correspond to inner products with a specified orthonormal basis $\phi_1, \phi_2, ...$ In the same way, linear operators may be associated with infinite matrices, two-dimensional arrays of complex numbers of the form

$$\begin{bmatrix} A_{11} & A_{12} & ... \\ A_{21} & A_{22} & ... \\ \vdots & \vdots & \ddots \end{bmatrix} \tag{4.12}$$

where the coefficients A_{mn} are the *matrix elements*

$$A_{mn} = (\phi_m, \hat{A}\phi_n) \tag{4.13}$$

of the operator $\hat{A}$ in the orthonormal basis $\phi_1, \phi_2, ...$ To see why this association is useful, suppose we wish to calculate vector elements for the vector $\hat{A}\psi$ that results from the

operation of a linear operator $\hat{A}$ on some given state vector ψ. In the orthonormal basis $\phi_1, \phi_2, ...$, we can calculate the vector elements of $\hat{A}\psi$ as

$$
\begin{aligned}
[\hat{A}\psi]_m = (\phi_m, \hat{A}\psi) &= (\phi_m, \hat{A} \sum_n \phi_n(\phi_n, \psi)) \\
&= \sum_n (\phi_m, \hat{A}\phi_n)(\phi_n, \psi) \\
&= \sum_n A_{nm}(\phi_n, \psi)
\end{aligned}
\tag{4.14}
$$

But this is none other than the matrix product

$$
\begin{bmatrix} (\phi_1, \hat{A}\psi) \\ (\phi_2, \hat{A}\psi) \\ \vdots \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & ... \\ A_{21} & A_{22} & ... \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} (\phi_1, \psi) \\ (\phi_2, \psi) \\ \vdots \end{bmatrix}
\tag{4.15}
$$

obtained using the matrix and vector representations for $\hat{A}\psi$, $\hat{A}$, and ψ in the $\phi_1, \phi_2, ...$ It is thus possible to draw a one-to-one correspondence between linear operators on a Hilbert space and infinite dimensional matrices. Matrix-vector multiplication corresponds to the action of an operator and arbitrary vector, while it is easily verified that matrix-matrix multiplication corresponds to the composition of two linear operators $\hat{A}$ and $\hat{B}$ to form a new operator $\hat{A}\hat{B}$.

A *Hermitian* operator is a specific type of linear operator which, in quantum mechanics, corresponds to a physically observable quantity. In a mathematical sense, the defining feature of a Hermitian operator is that the equality

$$
(\hat{A}\phi, \psi) = (\phi, \hat{A}\psi)
\tag{4.16}
$$

holds for all vectors ϕ and ψ in $\mathcal{H}$. In short, within an inner product expression, the choice of which vector a Hermitian operator acts on is independent of the result. In any matrix representation, it is easily verified that the matrix elements of a Hermitian operator satisfy the complex symmetry

$$
A_{mn} = A_{nm}^*.
\tag{4.17}
$$

This defining feature leads quickly to two additional characteristics of Hermitian operators which are particularly significant in quantum mechanics and which both deal with operator eigenvalues and eigenvectors. An *eigenvector* for a given linear operator $\hat{A}$ is any vector ϕ for which

$$
\hat{A}\phi = \alpha\phi
\tag{4.18}
$$

i.e. for which the result of the operator $\hat{A}$ acting on the vector is simply multiplication by a (possibly complex) scalar α. The characteristic constant α is called the *eigenvalue* of the

vector ϕ for the operator $\hat{A}$. A trivial example of an eigenvector for *any* linear operator is the zero vector $\mathbf{0}$ since for any linear operator $\hat{A}$ we have[7]

$$\hat{A}\mathbf{0} = \mathbf{0} \tag{4.19}$$

i.e. the zero vector $\mathbf{0}$ is an eigenvector of $\hat{A}$ with eigenvalue 0. This "trivial" eigenvector is usually of little interest to us, and when we speak of the eigenvectors of an operator, we generally refer to non-zero vectors only.

With these definitions, we quickly find that *every eigenvalue of a Hermitian operator $\hat{A}$ is a real number*. To see this, suppose that ϕ is a non-trivial eigenvector of $\hat{A}$ with eigenvalue α. (The statement is trivially satisfied for the zero vector $\mathbf{0}$.) By definition of a Hermitian operator, we have[8]

$$\alpha(\phi, \phi) = (\phi, \alpha\phi) = (\phi, \hat{A}\phi) = (\hat{A}\phi, \phi) = (\alpha\phi, \phi) \tag{4.21}$$

The linearity and conjugation properties of the inner product imply that

$$(\alpha\phi, \phi) = (\phi, \alpha\phi)^* = \alpha^*(\phi, \phi), \tag{4.22}$$

and since (again by the definition of the inner product) we know that for non-zero vectors $(\phi, \phi) > 0$, we conclude that $\alpha = \alpha^*$, i.e. that α is a real number.

A similar argument quickly shows that *eigenvectors of a Hermitian operator which have distinct eigenvalues are orthogonal*, i.e. their inner product is zero. Suppose that ϕ_1 and ϕ_2 are eigenvectors of a Hermitian operator $\hat{A}$ with non-zero eigenvalues λ_1 and λ_2. Then

$$\lambda_1(\phi_1, \phi_2) = (\hat{A}\phi_1, \phi_2) = (\phi_1, \hat{A}\phi_2) = \lambda_2(\phi_1, \phi_2). \tag{4.23}$$

Since λ_1 and λ_2 are different, non-zero numbers, this implies that $(\phi_1, \phi_2) = 0$, i.e. that the two vectors are orthogonal. (The condition is trivially satisfied for both the zero vector and for any non-zero eigenvector with eigenvalue zero).

The physical significance of these two properties of Hermitian operators (the reality of their eigenvalues and the orthogonality of degenerate eigenvectors) is highlighted by our next postulate.

Operators in L^2

Our second postulate tells us that a Hermitian operator exists for each physical observable. It does not, however, tell us how to identify such operators. In practice, each operator must be identified empirically, by determining which Hermitian operators give rise to the correct physical behavior. For our purposes, we take for granted the results of what would otherwise be a rather arduous process: in the Hilbert space L^2, *the operators corresponding to the position and momentum of a single particle are*

---

[7]Since for the zero vector we have $\phi + \mathbf{0} = \phi$ for any vector ϕ in $\mathcal{H}$, we see that

$$\hat{A}\phi + \mathbf{0} = \hat{A}\phi = \hat{A}(\phi + \mathbf{0}) = \hat{A}\phi + \hat{A}\mathbf{0}. \tag{4.20}$$

Subtracting the quantity $\hat{A}\phi$ from both sides gives the result.

given by

$$\hat{x} \equiv x\cdot$$

$$\hat{p} \equiv -i\hbar \frac{d}{dx} \tag{4.24}$$

Where the notation "$x\cdot$" indicates ordinary scalar multiplication by the coordinate x, and the symbol $\hbar$ represents the real-valued Planck's constant. From these two definitions, the operators corresponding to most physical observables can be calculated directly by simply replacing the classical quantities x and p with the corresponding quantum operators. For example, the kinetic energy operator takes in L^2 the form

$$\hat{T} = \frac{\hat{p}^2}{2M} = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} \tag{4.25}$$

where M is the particle mass. A particularly important example in both classical and quantum mechanics is the Hamiltonian for the system, the sum of the potential and kinetic energy operators. If the classical potential energy $V(x)$ of the system is a function only of the particle position, then the quantum potential energy operator $\hat{V}$ likewise (in L^2) corresponds simply to multiplication by the potential $V(x)$. In this case, the Hamiltonian takes the simple form

$$\hat{H} \equiv \hat{T} + \hat{V} = -\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x) \tag{4.26}$$

For example, suppose that our system wave function takes the form of the first Hermite polynomial $h_0(x)$ defined by Eq. (4.9):

$$\psi(x) = h_0(x) = \pi^{-\frac{1}{4}} e^{-\frac{x^2}{2}}. \tag{4.27}$$

Using the definitions above, we readily obtain

$$\hat{x}\psi(x) = x\psi(x)$$

$$\hat{p}\psi(x) = i\hbar\pi^{-1/4}xe^{-\frac{x^2}{2}}$$

$$\hat{T}\psi(x) = \frac{\hbar^2}{2M}\pi^{-1/4}\left[e^{-\frac{x^2}{2}} - x^2e^{-\frac{x^2}{2}}\right]$$

$$= \frac{\hbar^2}{2M}\left(1 - x^2\right)\psi(x)$$

$$\hat{H}\psi(x) = \frac{\hbar^2}{2M}\left(1 - x^2 - V(x)\right)\psi(x). \tag{4.28}$$

The last equality readily suggests the following observation: if $V(x)$ takes the harmonic form $V(x) = \frac{\hbar^2}{2M}x^2$, then $\psi(x)$ is an eigenvector of the Hamiltonian operator since

$$\hat{H}\psi = \frac{\hbar^2}{2M}\psi(x). \tag{4.29}$$

In fact, every Hermite function is an eigenvector of this particular Hamiltonian, with eigenvalues

$$\lambda_n = \frac{\hbar^2}{M}(n+1) \tag{4.30}$$

that increase linearly with n.

In L^2, we often refer to eigenvectors as *eigenfunctions* since each state vector takes the form of a function of x. It is easy to see that neither $\hat{x}$ nor $\hat{p}$ have any eigenfunctions in L^2. For function $f(x)$ to be in eigenfunctions of the $\hat{x}$ operator, we require that

$$\hat{x}f(x) = xf(x) = \lambda f(x) \tag{4.31}$$

for every point x between $-\infty$ and ∞. But for the statement to be true at any value of $x = x_o$, we must have $\lambda = x_o$. Clearly, this cannot be true for all values of x! Similarly, in order for $f(x)$ to be in eigenfunctions of the momentum operator $\hat{p}$, we must have

$$\hat{p}f(x) = -i\hbar\frac{d}{dx}f(x) = -i\hbar f'(x) = \lambda f(x). \tag{4.32}$$

This equation is satisfied for only one family of functions: $f(x) = \alpha e^{i\frac{\lambda}{\hbar}x}$, where α is an arbitrary constant. Unfortunately, no such function is square-integrable and so can never qualify as an element of L^2. Despite these apparently discouraging findings, we will see in the next section that both $\hat{x}$ and $\hat{p}$ possess well-behaved functions which *almost* qualify as eigenfunctions and play much the same role in quantum mechanics.

4.1.4 Third Posulate: Eigenvalues of Hermitian Operators

For any physical observable, the only values which are possible to obtain in a measurement are those in the spectrum of the corresponding Hermitian operator.

The physical plausibility of this postulate lies squarely on the the fact that eigenvalues of a Hermitian operator are strictly real numbers. This characteristic is what ensures in quantum theory that physical observables do not take on complex values. Nonetheless, from a classical perspective the claim is rather surprising. In fact, it is this postulate which from a physical perspective first strongly distinguishes classical and quantum mechanics. Whereas in classical mechanics most physical observables have a continuous range of values, in quantum mechanics many observables are allowed to have only specific discrete (or "quantized") values.

Atomic spin was one of the earliest studied examples of this so-called "quantization" effect in quantum mechanics. Experimentally, scientists observed that very small, electrically neutral particles (e.g., silver atoms) posessed a magnetic moment, as though the particle were spinning around an axis. By subjecting a beam of atoms to magnetic fields of varying directions, the magnitude and orientation of the magnetic dipole moment could be measured experimentally. However, instead of finding a continuously varying range of magnitudes and orientations (as one would expect for classical particles), scientists found that particles subject to an external magnetic field behaved as though every particle had a magnetic dipole of exactly the same magnitude and oriented either exactly parallel to the field or exactly opposite to it. According to the postulates of quantum mechanics, these two possible outcomes ("up" or "down" with respect to the magnetic field or " + 1″ and " − 1″ in short-hand notation) correspond to the two eigenvalues of a spin operator acting in the Hilbert space describing the state of the particles.

In such simple cases, the *spectrum* of a Hermitian operator consists simply of the set of all its eigenvalues. Our postulate then tell us that when we measure the corresponding physical property of the system, the value we observe must be contained within the spectrum of the Hermitian operator. Thus if an operator's spectrum consists of the numbers $\{-2, -1, 0, +1, +2\}$, then a measurement of the corresponding observable might return -1 or $+2$ but never -0.5 or $+3$. In such cases, we say that the spectrum of the operator is *discrete*, i.e. it possesses only a countable (even if infinite) range of possible values.

Even quantum mechanically, however, not all physical observables are "quantized" in the sense of having a discrete set of possible values. The position of a free (non-interacting) particle, for example, might take on any value in three-dimensional space; its momentum might take any value between positive and negative infinity. In quantum mechanics, these observables correspond to operators with *continuous* spectra.

As indicated above, the discrete spectrum of an operator consists of the set of all its eigenvalues. More formally, a number α is contained in the discrete spectrum of an operator $\hat{A}$ if (and only if) there exists a normalized vector ϕ such that

$$\hat{A}\phi = \alpha\phi. \tag{4.33}$$

Importantly, however, not all Hermitian operators have eigenvalues or eigenvectors. We will see later, for example, that the operators corresponding to the coordinate and momentum of a particle have no true eigenvalues. In such cases, the discrete spectrum of the operator is said to be empty. For every Hermitian operator, however, there do exist vectors which are âĂIJarbitrarily closeâĂİ to eigenvectors: families of normalized vectors $\psi_\epsilon^{(\alpha)}$ defined for some number α such that

$$\alpha\psi_\epsilon^{(\alpha)} \approx \hat{A}\psi_\epsilon^{(\alpha)} \tag{4.34}$$

to an arbitrary degree of precision as $\varepsilon \to 0$.[9] If such a family of vectors exists for a given number α, we say that α is contained in the spectrum of the operator $\hat{A}$. Note immediately that by this definition, every eigenvalue is contained in the spectrum since in this case the

approximation is satisfied exactly; thus the discrete spectrum is a subset of the spectrum. Those points α which satisfy the approximation (4.34) but are not true eigenvalues constitute the continuous spectrum.

Different operators have different types of spectra. Some operators (such as the spin operator discussed above) have purely discrete spectra; others (e.g. position and momentum) have purely continuous spectra; still others have both discrete and continuous contributions. Later, when we learn how to construct mathematically the operators corresponding to a given physical observable, we will be able to predict an operator's spectrum *a priori*.

Just as in the discrete case, it is straightforward to show that all elements in the continuous spectrum of a Hermitian operator must be real numbers. Similarly, just as eigenvectors corresponding to different eigenvalues are orthogonal to one another, vectors $\psi_\epsilon^{(\alpha)}$ and $\psi_\epsilon^{(\beta)}$ corresponding to two different points α and β in the spectrum of $\hat{A}$ approach orthogonality in the limit that $\epsilon \to 0$. Thanks to these similar properties, the "almost" eigenvectors $\phi_\epsilon^{(\alpha)}$ corresponding to points in the continuous spectrum of a Hermitian operator behave in much the same way as the true eigenvectors corresponding to points in the discrete spectrum. For this reason, in what follows we will generally work only with discrete eigenvectors and eigenvalues, even when discussing operators having continuous spectra. Although not formally correct, this simplified treatment is substantially more straightforward in its development and is directly analogous to the more nuanced statement in terms of continuous spectra.

This definition of the spectrum of an operator completes our formal statement of the thid postulate. As of yet, although we know what set of values may be observed in a measurement, we have no indication of how the physical state of the system determines which value we measure. From our earlier postulates, of course, we know that the information must somewhere be contained in the state vector; but so far we do not know how to access it. As might be surmised already, the phsyical states represented by the eigenvectors of a Hermitian operator are specially linked to the observation of their corresponding eigenvalues in experiment. The reality of Hermitian eigenvalues (or points in a continuous spectrum) and the orthogonality of Hermitian eigenvectors (or "almost" eigenvectors for operators with continuous spectra) will then be of special significance since these features will allow us to decompose arbitrary state vectors into contributions from different eigenstates.

"Eigenfunctions" for $\hat{x}$ and $\hat{p}$

We noted in the last section that the operators $\hat{x}$ and $\hat{p}$ possess no true eigenfunctions in L^2. The discrete spectra for these two operators are thus empty; the range of possible experimental values for these two observables is thus determined entirely by

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[9] The approximate equality is meant in the sense that the quantity $\|\hat{A}\psi_\varepsilon^{(\alpha)} - \alpha\psi_\varepsilon^{(\alpha)}\|$ can be made arbitrarily small by choosing a suitably small value of ε. This is not the usual definition of the spectrum of an operator, but is equivalent and is presented here for its relative transparency. Importantly, this definition applies only to the spectrum of Hermitian operators. See Jordan for a more standard definition of the operator spectrum and Stone for a detailed treatment.

the continuous spectrum. In fact, for both operators, the continuous spectrum covers the entire real line.

To see this, consider the normalized family of step functions defined by

$$d_{x_o}^{(\epsilon)}(x) = \begin{cases} \frac{1}{\sqrt{\epsilon}}, & x_o - \frac{\epsilon}{2} \le x \le x_o + \frac{\epsilon}{2} \\ 0, & otherwise. \end{cases} \tag{4.35}$$

for any real numbers x_o and ϵ. As $\epsilon \to 0$, we see that

$$\hat{x} d_{x_o}^{(\epsilon)}(x) \approx x_o d_{x_o}^{(\epsilon)}(x) \tag{4.36}$$

since

$$\|\hat{x} d_{x_o}^{(\epsilon)}(x) - x_o d_{x_o}^{(\epsilon)}(x)\|^2 = \int_{-\infty}^{\infty} \left(x d_{x_o}^{(\epsilon)}(x) - x_o d_{x_o}^{(\epsilon)}(x) \right)^2 dx = \frac{\epsilon^2}{12}. \tag{4.37}$$

Moreover, if $|x_1 - x_2| > \epsilon$, then the functions $d_{x_1}^{(\epsilon)}(x)$ and $d_{x_2}^{(\epsilon)}(x)$ are both normalized and orthogonal.

Similarly, consider the family of functions

$$\rho_{p_o}^{(\epsilon)}(x) = \left(\frac{2}{\pi \epsilon} \right)^{1/2} e^{-ip_o x} \frac{\sin\left(\frac{\epsilon}{2} x \right)}{x}. \tag{4.38}$$

As $\epsilon \to 0$, this family of normalized functions serve as approximate eigenfunctions for the momentum operator, with approximate eigenvalues $\hbar p_o$. In fact, the vector norm $\|\hat{p} \rho_{p_o}^{(\epsilon)}(x) - \hbar p_o \rho_{x_o}^{(\epsilon)}(x)\|^2$ approaches zero as $\frac{\epsilon^2}{12}$, just as we saw for the functions $d_{x_o}^{(\epsilon)}(x)$ with the $\hat{x}$ operator.[a]

Given this behavior, it is natural to ask what happens to the functions themselves as $\epsilon \to 0$. Indeed, one sometimes sees the limit

$$\delta_{x_o}(x) \equiv \lim_{\epsilon \to 0} \left[d_{x_o}^{(\epsilon)}(x) \right]^2 \tag{4.39}$$

used to define the *Dirac delta function*, a somewhat mystical function with the property that

$$\int_{-\infty}^{\infty} dx \, \delta_{x_o}(x) f(x) = f(x_o) \tag{4.40}$$

for any function $f(x)$. Unfortunately, no true function satisfies this criterion since (just as in the limit above) it would take on an infinite value at $x = x_o$. Similarly, we often speak informally of the plane waves $e^{-ip_o x}$ noted in the last text box as eigenfunctions of $\hat{p}$. However, the plane waves are not square-integrable and thus are not valid elements of L^2.

The proper mathematical role for both the Dirac delta functions and the plane waves in L^2 is as a tunable family of distributions. A *distribution* is a particular type of mapping which matches vectors in L^2 with complex numbers. For example, the Dirac delta distribution maps every function $f(x)$ to its value at x_o:

$$\int_{-\infty}^{\infty} dx \delta_{x_o}(x) f(x) \equiv f(x_o) \tag{4.41}$$

Similarly, the Fourier integral distribution maps each function $f(x)$ to its Fourier transform $\tilde{f}(k)$ evaluated at $k = k_o$:

$$\tilde{f}(k_o) \equiv \int_{-\infty}^{\infty} dx e^{ik_o x} f(x). \tag{4.42}$$

It is to these two distributions that the near-eigenstates of the $\hat{x}$ and $\hat{p}$ operators converge in the sense that

$$\int_{-\infty}^{\infty} dx \delta_{x_o}(x) f(x) = f(x_o) = \lim_{\epsilon \to 0} \epsilon^{\frac{1}{2}} \left(d_x^{(\epsilon)}, f \right) \tag{4.43}$$

$$\int_{-\infty}^{\infty} dx e^{ik_o x} f(x) = \tilde{f}(k_o) = \frac{1}{\sqrt{2\pi}} \lim_{\epsilon \to 0} \epsilon^{\frac{1}{2}} \left(\rho_{k_o}^{(\epsilon)}, f \right). \tag{4.44}$$

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[a]These properties are perhaps easiest to verify in the Fourier domain where $\rho_{p_o}^{(\epsilon)}(x)$ is converted to simply $d_{p_o}^{(\epsilon)}(k)$.

4.1.5 The Fourth Postulate: Probabilities

In any experimental measurement of an observable a corresponding to Hermitian operator $\hat{A}$ with a purely discrete spectrum, the probability of obtaining a value between α_1 and α_2 is given by

$$P(\alpha_1 \leq a \leq \alpha_2) = \sum_{\alpha_1 \leq \lambda_n \leq \alpha_2} |(\phi_n, \psi)|^2 \tag{4.45}$$

where the vectors $\phi_1, ..., \phi_n, ...$ form a complete, orthonormal set of eigenvectors for the operator $\hat{A}$ and $\lambda_1, ..., \lambda_n, ...$ are the corresponding eigenvalues.

Given a Hermitian operator $\hat{A}$, the last postulate identifies for us the possible values we might obtain in a measurement of the corresponding observable - namely, the eigenvalues of $\hat{A}$. Given a state vector ψ, our fourth postulate identifies the probabilities of obtaining each possible result - namely the squared projection of the state vector ψ onto the corresponding eigenvector ϕ_n. This fourth postulate begins finally to make concrete the implication of our

first postulate that the state vector ψ contains information regarding the physical state of our system.

The physical implications of these postulates are indeed profound. Recall that our first postulate stated that the state vector ψ contains all physical information which can be known about the system. Our present postulate implies that, even with complete knowledge of the state vector ψ, the outcome of any given experiment can be predicted only in a statistical sense. In any given measurement, many different outcomes are possible, even when the state vector ψ is known in advance. Only if the state vector ψ is itself an eigenvector ϕ_n (so that $P(\alpha_1 \leq a \leq \alpha_2)$ =1 if $\alpha_1 \leq \lambda_n \leq \alpha_2$ and zero otherwise) can the result of an experiment be predicted with absolute confidence. Even in this case, however, the values of some physical observables must remain uncertain. Indeed, certain pairs of physical observables - most notably, the position operator $\hat{x}$ and the momentum operator $\hat{p}$ - share no eigenvectors in common. Thus if the state vector for a particle is such that its position is known precisely, its momentum must be highly uncertain. This is but one example of Heisenberg's celebrated *uncertainty principle*.

The physical, and indeed philosophical, implications of the uncertainty inherent in quantum mechanics remains a subject of debate today.What is clear, however, is that no other physical theory captures the workings of the universe around us in such great detail and with such great accuracy as has been achieved by quantum theory. Regardless of the philosophical consequences, quantum theory has tremendously improved our ability to describe and predict physical processes.

As should be expected by this point, the validity of these physical assertions rests squarely upon the mathematical properties of Hilbert spaces and, in particular, upon the unique characteristics of Hermitian operators. In the case of a Hermitian operator $\hat{A}$ with a purely discrete spectrum (as in our statement of the postulate above), the critical mathematical statement is that *the eigenvectors of any Hermitian operator form a complete basis for the entire Hilbert space*. More explicitly, this means that any state vector ψ can be written exactly as linear combination of the form

$$\psi = \sum_n (\phi_n, \psi)\phi_n \tag{4.46}$$

where $\phi_1, \phi_2, ...$ are the (orthonormal) eigenvectors of some Hermitian operator $\hat{A}$. Once again, the mathematical properties of Hermitian operators are found in quantum mechanics to have profound physical implications. Indeed, were the set of eigenvectors $\phi_1, \phi_2, ...$ not a complete set, then according to our postulate the probability $P(-\infty \leq a \leq \infty)$ of obtaining *any* value would be less than one. In some measurements, the system would apparently not exist!

Although simple to state, the assertion that an expansion of the form (4.46) always exists is not simple to demonstrate. Moreover, both the mathematical statement ande the physical postulate are more complicated to state (let alone prove) in the case of an operator $\hat{A}$ whose continuous spectrum is nonempty. In the continuous case, the corresponding expressions involve an integral over contributions from different points in the spectrum of the operator

$\hat{A}$. As neither the proof of the expression (4.46) nor the distinction between discrete and continuous spectra play a material role in our development of quantum mechanics, we omit them here. For a concise introduction to these topics see Thomas Jordan's excellent monograph *Linear Operators for Quantum Mechanics*; for a more detailed discussion, see M. H. Stone's authoritative *Linear Transformations in Hilbert Space*.

Before we move on to our next postulate, it is instructive to consider what happens when we calculate the *expectation value* or average of a given operator $\hat{A}$. Using our cumulative distribution function $P(\alpha_1 \leq a \leq \alpha_2)$, the expectation value is in general calculated as

$$\langle a \rangle = \int_{-\infty}^{\infty} \alpha \, dP(-\infty \leq a \leq \alpha) \tag{4.47}$$

where the integral is to be understood in the Riemann-Stieltjes sense

$$\int_{\alpha}^{\beta} g(x) dF(x) = \lim_{N \to \infty} \sum_{n=1}^{N} g(x_n) \left[F(x_n) - F(x_{n-1}) \right] \tag{4.48}$$

where the sequence $x_0 < x_1 < \dots < x_N$ divides the interval $[\alpha, \beta]$ into increasingly smaller subintervals. When $P(-\infty \leq a \leq \alpha)$ is a differentiable function of α, this integral is equivalent to

$$\langle a \rangle = \int_{-\infty}^{\infty} \alpha \frac{dP}{d\alpha} d\alpha. \tag{4.49}$$

This is the form obtained for operators of purely continuous spectra. For operators with purely discrete spectra, the excitation value is instead calculated by expanding the cumulative distribution function $P(-\infty \leq a \leq \alpha)$ in terms of the eigenstates $\phi_1, \phi_2, \dots$ to obtain from Eq. (4.48):

$$\langle a \rangle = \sum_{n} \lambda_n |(\phi_n, \psi)|^2. \tag{4.50}$$

But since the vectors ϕ_n are both complete and orthonormal, this sum is equivalent to

$$\langle a \rangle = \left(\sum_{n} \phi_n^* \right) \hat{A} \left(\sum_{n} \phi_n (\phi_n, \psi) \right) = (\psi, \hat{A}\psi). \tag{4.51}$$

In fact, the final equality is valid in general, for operators with both discrete and continuous spectra. This result will be extremely useful to us in calculating the properties of physical systems.

Probabilities for continuous spectra

Although a general discussion of operators with continuous spectra is beyond the scope of our discussion here, we can provide a brief explanation of how probabilities are calculated for the $\hat{x}$ and $\hat{p}$ operators. Our first requirement is to attain an expansion analogous to Eq. (4.46) in terms of $\hat{x}$ and $\hat{p}$ "eigenstates." Beginning with the $\hat{x}$

operator, consider the expansion

$$f(x) \approx f_N(x) = \sum_{n=0}^{N} d_{x_n}^{(\epsilon_N)}(x) \left(d_{x_n}^{(\epsilon_N)}, f \right) \tag{4.52}$$

with N an integer, L a real constant, $\epsilon_N = \frac{2L}{N}$, and $x_n = L\left(\frac{2n}{N} - 1\right)$. As $L \to \infty$ and $N \to \infty$, the approximation becomes exact for any function $f(x)$ in L^2 as the functions $d_{x_n}^{(\epsilon_N)}(x)$ approximate each segment of $f(x)$ on smaller and smaller intervals.

It should come as no surprise, then, that we can approximate the probability $P(\alpha_1 \leq x \leq \alpha_2)$ of finding a particle with a coordinate between α_1 and α_2 as a sum over the contributions from each approximate eigenfunction:

$$P(\alpha_1 \leq x \leq \alpha_2) \approx \sum_{\alpha_1 \leq x_n \leq \alpha_2} \left| \left(d_{x_n}^{(\epsilon_N)}, \psi \right) \right|^2. \tag{4.53}$$

Indeed, for $\alpha_1, \alpha_2 \in [-L, L]$, the approximation becomes exact as $N \to \infty$, converging to the integral

$$P(\alpha_1 \leq x \leq \alpha_2) = \lim_{N \to \infty} \sum_{\alpha_1 \leq x_n \leq \alpha_2} |\psi(x_n)|^2 \epsilon_N = \int_{\alpha_1}^{\alpha_2} |\psi(x)|^2 dx. \tag{4.54}$$

Similarly, by expanding in terms of approximate momentum eigenfunctions

$$f(x) \approx \sum_{n=0}^{N} \rho_{k_n}^{(\epsilon_N)}(x) \left(\rho_{k_n}^{(\epsilon_N)}, f \right), \tag{4.55}$$

we can calculate the probability of observing a momentum value between α_1 and α_2 as the integral

$$P(\alpha_1 \leq p \leq \alpha_2) = \lim_{N \to \infty} \sum_{\alpha_1 \leq \hbar k_n \leq \alpha_2} \left| \tilde{\psi}(k_n) \right|^2 \epsilon_N = \int_{\alpha_1/\hbar}^{\alpha_2/\hbar} \left| \tilde{\psi}(k) \right|^2 dk. \tag{4.56}$$

In fact, these results are a special case of a more general principle regarding the spectra of Hermitian operators. Rigorous analysis shows that for every Hermitian operator $\hat{A}$ there exists a family of Hermitian *spectral projection operators* $\hat{E}_\alpha$ defined for every real number α such that

1. $\|\hat{E}_\alpha \psi\| \leq \|\psi\|$ for every vector ψ and every real number $\hat{\alpha}$.

2. $\hat{E}_\alpha^2 = \hat{E}_\alpha$.

3. If $\alpha \leq \beta$, then $\hat{E}_\alpha \hat{E}_\beta = \hat{E}_\alpha = \hat{E}_\beta \hat{E}_\alpha$.

4. For any $\epsilon > 0$, we have $\lim_{\epsilon \to 0} \hat{E}_{\alpha + \epsilon} \psi = \hat{E}_\alpha \psi$ for any ψ and all α.

5. For any vector ψ, we have $\lim_{\alpha \to -\infty} \hat{E}_\alpha \psi = 0$, and $\lim_{\alpha \to \infty} \hat{E}_\alpha \psi = \psi$.

6. For any vectors ψ and ϕ, we have

$$\left(\phi, \hat{A}\psi \right) = \int_{-\infty}^{\infty} \alpha d \left(\phi, \hat{E}_\alpha \psi \right). \tag{4.57}$$

In the last expression, the integral is to be understood as the Riemann-Stieltjes integral defined in the main text.

With this definition, we can provide a general statement of our postulate. For any Hermitian operator $\hat{A}$ – whether its spectrum is continuous, discrete, or mixed – the probability of measuring the observable a between α_1 and α_2 is given by

$$P(\alpha_1 \leq p \leq \alpha_2) = \int_{\alpha_1}^{\alpha_2} d\|\hat{E}_\alpha \psi\|^2 \tag{4.58}$$

where ψ is the wavefunction of the system. Given our results above, the form for the spectral family of operators for $\hat{x}$ and $\hat{p}$ are easily verified to be defined by the behavior

$$\hat{E}_{x_o} \psi(x) = \psi(x)\Theta(x_o - x) \tag{4.59}$$

$$\hat{E}_{p_o} \psi(x) = \frac{1}{2\pi} \int_{-\infty}^{p_o/\hbar} e^{-ikx} \tilde{\psi}(k) dk \tag{4.60}$$

where $\Theta(x)$ is a step function defined to be 0 for negative values and 1 for positive values.

4.1.6 The Fifth Postulate:

In any experimental measurement of an observable a corresponding to Hermitian operator $\hat{A}$, the state of the system immediately following the measurement is given by the normalized state vector

$$\psi' \propto \sum_{\lambda_n = \alpha} (\phi_n, \psi)\phi_n \tag{4.61}$$

where α is the value of the observable a actually observed in the experiment, $\phi_1, ..., \phi_n, ...$ form a complete, orthonormal set of eigenvectors for the operator $\hat{A}$, and $\lambda_1, ..., \lambda_n, ...$ are the corresponding eigenvalues.
If the spectrum of the operator $\hat{A}$ is non-degenerate at the point α (that is, if there is only one distinct eigenvector ϕ_n with eigenvalue α), then the state vector for the system after the measurement is simply

$$\psi' = \phi_n. \tag{4.62}$$

Our last two postulates have allowed us to describe statistically the outcome of any given measurement. Our next postulate describes the effect of an experimental measurement on the system itself. At one level, the postulate is unsurprising. It merely states that when we conduct an experiment on a physical system, we inevitably perturb it from its pre-experiment state. What is perhaps surprising is that the postulate presents this experimental perturbation as a fundamental part of the measurement process with a precisely defined outcome on the state of the system. Moreover, this outcome is independent of our experimental design or the care with which we conduct our measurement. Fundamentally, these concept are closely tied to the Heisenberg uncertainty principle described in the last postulate.

A Physical Example

A concrete physical example may help to clarify the content of the postulate. Suppose we wish to find the position of a single atom on a flat surface. One possible means of locating the atom is to scan across the surface with a tightly-focused laser beam, resonant with one of the absorption frequencies of the atom. When we detect fluorescent signal emitted at the resonant atomic frequency, we know that the laser beam is focused on the atom. The spatial resolution of this technique is limited by the finite spot size (proportional to the wavelength) of our laser beam. Thus a visible laser could identify the position of the atom to within a few hundred nanometers, while an x-ray source could (in principle) locate the atom to within a few Ångströms.

Now consider the effects of this measurement process on the atom itself. While laser excitation gives rise to fluorescence and alerts us to the position of the atom, it also gives rise to local heating effects and scattering events that can displace the atom from its initial position. In fact, the amount of kinetic energy that may be imparted to the atom is inversely proportional to the wavelength. Thus while a beam of relatively low-energy visible light may only weakly perturb the atom, a high-energy x-ray beam is quite likely to send the atom hurtling through space far from its initial position.

In this simple, hypothetical example, we see that our efforts to determine the location of the atom more precisely using a high-energy excitation source also give rise to greater uncertainty in the momentum of the atom following the measurement. For this particular experimental setup, it is thus impossible to know both the position and momentum of the atom with high certainty. The striking feature of our fifth postulate is that it asserts that this inverse uncertainty relationship is a fundamental feature of physical systems, independent of our experimental details. No matter how carefully we conduct our measurement, how well calibrated are our instruments, or how cleverly we design our experiment to avoid perturbation, we will ultimately face the same limiting uncertainty relationship.

To see how these conclusions follow from this postulate just stated, let us consider the same localization problem from a strictly quantum mechanical perspective, with no reference to laser beams, spot size, or any other knowledge of how the experiment is actually conducted. We specify only that at the start of the experiment the state vector ψ of the system is such that the expected momentum value is zero in both the x and y dimensions

and that there is equal probability of observing the atom at any point on the surface. The probability density $p_{\boldsymbol{x}}(x, y)$ for observing the particle in the vicinity of the point (x, y) is then simply the flat distribution

$$p_{\boldsymbol{x}}(x, y) = \frac{1}{A} \tag{4.63}$$

where A is the total area of the surface. Now suppose that after conducting a measurement on the system we have identified that the particle is located at the point (x_o, y_o) to within an error of $\pm \epsilon/2$ in each dimension.[10] As described in detail in the text box, after projecting the wave function onto the $\hat{x}$ and $\hat{y}$ "eigenvectors" having eigenvalues within the intervals $[x_o - \epsilon/2, x_o + \epsilon/2]$ and $[y_o - \epsilon/2, y_o + \epsilon/2]$, we obtain a modified probability density

$$p_{\boldsymbol{x}}(x, y) = \begin{cases} \frac{1}{\epsilon^2}, & \begin{array}{l} x \in [x_o - \epsilon/2, x_o + \epsilon/2] \\ y \in [y_o - \epsilon/2, y_o + \epsilon/2] \end{array} \\ 0, & otherwise. \end{cases} \tag{4.64}$$

The corresponding probability density $p_{\boldsymbol{p}}(p_x, p_y)$ is given by

$$p_{\boldsymbol{p}}(p_x, p_y) = \frac{4}{\pi^2 \epsilon^2} \frac{\sin^2\left(\frac{\epsilon}{2} p_x\right)}{p_x{}^2} \frac{\sin^2\left(\frac{\epsilon}{2} p_y\right)}{p_y{}^2}. \tag{4.65}$$

As our experimental error ϵ decreases, the position probability density $p_{\boldsymbol{x}}(x, y)$ becomes increasingly sharply peaked around the point (x_o, y_o), while the momentum probability density $p_{\boldsymbol{p}}(p_x, p_y)$ broadens in the same proportion. We thus obtain from a completely generic argument - independent of the design of our experiment - the same conclusion we reached in our hypothetical laser fluorescence experiment: that any measurement which precisely determines the position of a particle must necessarily introduce correspondingly large uncertainty into its momentum.

Simultaneous Measurability

Of course this inverse relationship between certainty and position and momentum is but one example of the far-reaching consequences of this postulate. An unlimited number of similar "uncertainty relations" could be identified: position and momentum, angular momentum along orthogonal axes, position and energy. This begs the question: under what circumstances is it possible for two different observables a and b to simultaneously take on precisely determined values?

In part, this question is already answered by our last postulate. Under our fourth postulate, we saw that the value of an observable a can be predicted with certainty only of

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[10]A more realistic analysis would allow for "soft" error bounds and, in most experimental setups, radial symmetry. For example, a Gaussian probability density would be realistic for laser-based experiment. Our use of sharp cutoffs and rectangular error bounds is purely for convenience; the physical implications are independent of the detailed functional form.

the wavefunction of the system is an eigenvector of this corresponding Hermitian operator $\hat{A}$. By extension, a quantum state ψ can have well-defined values of both a and b only if ψ is an eigenstate of both $\hat{A}$ and $\hat{B}$. Our fifth postulate adds to this condition the assertion that the measured value of an observable a can be unaffected by the measurement of an additional observable b if, and only if, the state vector ψ of the system is an eigenvector of both $\hat{A}$ and $\hat{B}$. For if the initial state ψ of the system is an eigenvector of $\hat{A}$ with eigenvalue α, then measurement of the observable a will yield the definite value α and will leave the state of the system unperturbed since if $\{\phi_1, \phi_2, ...\}$ is the orthonormal set of eigenvectors of $\hat{A}$, then

$$\psi' = \sum_{\lambda_n = \alpha} \phi_n (\phi_n, \psi) = \psi. \tag{4.66}$$

Likewise, if ψ is an eigenvector of $\hat{B}$ with eigenvalue β, then measurement of the observable b leaves the state of the system unchanged. Thus measurement of the quantities a and b may be repeated indefinitely with no perturbation of the system. On the other hand, if the initial state vector ψ is not a simultaneous eigenstate of $\hat{A}$ and $\hat{B}$, then measurement of one observable will necessarily influence the results of a measurement on the other observable.

Commuting Operators

In light of these observations, it is natural to ask under what circumstances a vector ψ can be a simultaneous eigenvector of two operators $\hat{A}$ and $\hat{B}$. It turns out that this is possible if and only if the operators $\hat{A}$ and $\hat{B}$ *commute* with respect to the vector ψ. Two operators are said to commute if

$$\hat{A}\hat{B} = \hat{B}\hat{A}, \tag{4.67}$$

that is, if the order of operations of $\hat{A}$ and $\hat{B}$ does not matter. The operator

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{4.68}$$

is called the *commutator* of the two operators. By definition, $\hat{A}$ and $\hat{B}$ commute if and only if their commutator is zero.

   To see how commutation is related to the existence of simultaneous eigenstates, suppose that the state ψ is a simultaneous eigenstate of both $\hat{A}$ and $\hat{B}$ with eigenvalues α and β. Then

$$\hat{A}\hat{B}\psi = \alpha\beta\psi = \hat{B}\hat{A}\psi. \tag{4.69}$$

Thus, at least with respect to action on the vector ψ, the operators $\hat{A}$ and $\hat{B}$ commute.

   On the other hand, suppose that the operators $\hat{A}$ and $\hat{B}$ possess pure point spectra and commute for all vectors. We claim that there exists a complete, orthonormal set of vectors $\{\psi_1, \psi_2, \psi_3, ...\}$ which are eigenvectors of both $\hat{A}$ and $\hat{B}$. The proof of this assertion is somewhat complicated but is worth going through in detail since it introduces several additional concepts important in the mathematics of quantum mechanics.

Note first that if ψ is an eigenvector of $\hat{A}$ with eigenvalue α, then the vector $\hat{B}\psi$ is also an eigenvector of $\hat{A}$ with eigenvalue α since

$$\hat{A}(\hat{B}\psi) = \hat{B}\hat{A}\psi = \alpha(\hat{B}\psi). \tag{4.70}$$

If the eigenvalue α is non-degenerate, then necessarily $\hat{B}\psi \propto \psi$, and ψ is also an eigenvector of $\hat{B}$ with some eigenvalue β. If all the eigenvalues α_n of $\hat{A}$ were non-degenerate, then we would be done; the eigenvectors ϕ_n would in this case already form a complete, orthonormal set of simultaneous eigenvectors of $\hat{A}$ and $\hat{B}$.

If the eigenvalue α is degenerate, then let $\phi_{n_1}, \phi_{n_2}, ...$ be those vectors from the orthonormal basis of eigenvectors of $\hat{A}$ with eigenvalue α. The set of all linear combinations of this orthonormal set of vectors defines a *subspace $\mathcal{M}_\alpha$* of the Hilbert space $\mathcal{H}$: a set of vectors contained in a Hilbert space which themselves form a Hilbert space, being closed under addition and scalar multiplication and using the same inner product as the parent space $\mathcal{H}$.[11] In fact, any vector in this subspace is also an eigenvector of $\hat{A}$ with eigenvalue α. Conversely, the set of all linear combinations of the orthonormal eigenvectors $\{\phi_n | n \notin \{n_1, n_2, ...\}\}$ also forms a subspace $\mathcal{M}_\alpha^\perp$ whose elements are orthogonal to every vector in $\mathcal{M}_\alpha$. The subspace $\mathcal{M}_\alpha^\perp$ is termed the *orthogonal complement* of $\mathcal{M}_\alpha$.

For any vector χ in the parent Hilbert space $\mathcal{H}$, we now define the *projection of χ onto the subspace $\mathcal{M}_\alpha$* to be the vector

$$\hat{I}_\alpha \chi = \sum_k \phi_{n_k}(\phi_{n_k}, \chi). \tag{4.71}$$

Inherent in this definition is the definition of a *projection operator $\hat{I}_\alpha$* which projects vectors onto the subspace $\mathcal{M}_\alpha$. For every vector χ, the projection operator $\hat{I}_\alpha$ thus retains those components that are contained in the subspace $\mathcal{M}_\alpha$. Note that projection onto the subspace $\mathcal{M}_\alpha$ is precisely the operation prescribed in our first postulate for determining the post-measurement state of our system. Conversely the projection operator $\hat{I}_\alpha^\perp \equiv \hat{I} - \hat{I}_\alpha$ is easily verified to perform the equivalent projection onto the orthogonal subspace $\mathcal{M}_\alpha^\perp$. It is easily verified that both $\hat{I}_\alpha$ and $\hat{I}_\alpha^\perp$ are both Hermitian and idempotent (i.e. $\hat{I}_\alpha^2 = \hat{I}_\alpha$). In fact, these two characteristics are the defining feature of a projection operator.

Now suppose that the vector χ is an eigenvector of $\hat{B}$ with eigenvector β. We claim that the vector $\hat{I}_\alpha \chi$ is also an eigenvector of $\hat{B}$ with eigenvector β. For χ can always be decomposed as

$$\chi = \hat{I}_\alpha \chi + \hat{I}_\alpha^\perp \chi. \tag{4.72}$$

Since $\hat{I}_\alpha \chi$ is contained in the subspace $\mathcal{M}_\alpha$, the commutation of $\hat{A}$ and $\hat{B}$ imply that $\hat{B}\hat{I}_\alpha \chi$ is also contained in $\mathcal{M}_\alpha$. The converse argument using the projection operator $\hat{I}_\alpha^\perp$ shows

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[11]If the set $\{\phi_{n_1}, \phi_{n_2}, ...\}$ contains only a finite number N of vectors, this should technically be termed an *N-dimensional unitary space*.

the $\hat{B}\hat{I}_\alpha^\perp \chi$ is also contained in the orthogonal complement $\mathcal{M}_\alpha^\perp$. As a result, by applying the operator $\hat{I}_\alpha$ to the eigenvector equation $\hat{B}\chi = \beta\chi$, we obtain

$$\hat{B}\hat{I}_\alpha \chi = \beta\hat{I}_\alpha \chi. \tag{4.73}$$

Thus $\hat{I}_\alpha \chi$ is an eigenvector of both $\hat{A}$ and $\hat{B}$. By repeating this procedure for every eigenvector χ_n of $\hat{B}$, and if necessary using the Graham-Schmidt orthogonalization procedure, we can construct an orthonormal set of vectors $\{\psi_1, \psi_2, ...\}$ that are eigenvectors of $\hat{B}$ and span the subspace $\mathcal{M}_\alpha$. Repeating this procedure for every eigenvalue ϕ_n of $\hat{A}$, this set can be extended to span the entire Hilbert space $\mathcal{H}$.

Bra-Ket Notation

Finally, a word on notation. The notation we have used so far for representing vectors and inner products is commonly adopted in the mathematics literature. In the physics and chemistry literature, an alternative notation which is in some cases more convenient (although also in some cases less precise) is widely accepted. In this bra-ket notation, a vector ψ is represented by a left-facing angular bracket $|\psi\rangle$, termed a *ket*. Thus the symbols $|\psi\rangle$, $|a\rangle$, and $|3\rangle$ are all understood immediately to refer to vectors in some Hilbert space $\mathcal{H}$. In complement, we denote by right-facing angular brackets $\langle \ |$ the distribution defined by taking the inner product with some specific vector in the Hilbert space. (Recall that we have already been introduced to distributions in our discussion of the Dirac delta function.) These distributions are referred to as *bras*. For example, the bra $\langle \phi|$ is understood to represent the distribution defined by

$$\langle \phi| \ \psi\rangle = (\phi, \psi) \tag{4.74}$$

for every vector $|\psi\rangle$ in $\mathcal{H}$.[12]

   The major utility of bra-ket notation is in defining certain operators, in particular the projection operators $\hat{I}_\alpha$ referred to in the last section. Using the definitions just presented, we have immediately in bra-ket notation

$$\hat{I}_\alpha = \sum_{\lambda_n=\alpha} |\phi_n\rangle \langle \phi_n| \,. \tag{4.75}$$

In what follows, we will alternate between these two forms of notation as convenience dictates. So long as both forms are used self-consistently, there is little danger of ambiguity.

Projection Operators for Position and Momentum

   In order to calculate the post-measurement probability densities described in Eqs.(4.64) and (4.65), we must first provide a more general statement of the postulate accounting for operators with continuous spectra. If $\hat{E}_\alpha$ is the spectral projection operator described in the last text box for the operator $\hat{A}$, our fifth postulate states that the post-measurement

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[12]One sometimes hears the bra $\langle \psi|$ referred to as the complex conjugate of the ket $|\psi\rangle$. Formally, this is incorrect: in fact, $\langle \psi|$ is not even an element of the same Hilbert space as is $|\psi\rangle$.

state of the system is given by

$$\psi' \propto \left(\hat{E}_{\alpha+\frac{\epsilon}{2}} - \hat{E}_{\alpha-\frac{\epsilon}{2}} \right) \psi \tag{4.76}$$

where ψ is the initial state of the system, α is the measured value, and $\pm\frac{\epsilon}{2}$ is the error on the measurement.[a] This statement includes the case of observables with discrete spectra since it is easily verified from the definition of $\hat{E}_\alpha$ that for an operator $\hat{A}$ with a purely discrete spectrum

$$\hat{E}_\alpha = \sum_{\lambda_n \leq \alpha} |\phi_n\rangle \langle\phi_n| \tag{4.77}$$

where the vectors $\phi_1, \phi_2, \ldots$ are the orthonormal eigenvectors of $\hat{A}$ with eigenvalues $\lambda_1, \lambda_2, \ldots$. In the case of a measurement on the x coordinate, our previous results on the form for the operator $\hat{E}_x$ in L^2 indicate that for an initial wave function $\psi(x)$, the post-measurement state of the system is given by simply

$$\psi'(x) = \begin{cases} \dfrac{\psi(x)}{\int_{x_o-\frac{\epsilon}{2}}^{x_o+\frac{\epsilon}{2}} |\psi(x)|^2} dx, & x_o - \frac{\epsilon}{2} \leq x \leq x_o + \frac{\epsilon}{2} \\ 0, & otherwise. \end{cases} \tag{4.78}$$

To analyze the problem given in the text, we work in a two-dimensional version of L^2: the Hilbert space of all square-integrable functions of two real variables x and y. All the results we previously obtained in the one-dimensional position space of functions of a single real variable transfer directly. In the new space, we have two position operators, one for the x coordinate and one for the y coordinate. The corresponding momentum operators in each dimension take the form of partial derivatives with respect to x or y.

To obtain the starting probability density of Eq. (4.63), we take the initial wave function for system to be simply

$$\psi(x, y) = \frac{1}{A^{\frac{1}{2}}} \tag{4.79}$$

for coordinates (x, y) on the surface and zero elsewhere. Here A is the area of the surface. The expected value for the momentum in both the x and y dimensions is easily found to be zero, as required. A simple extension of our one-dimensional analysis implies immediately that the post-measurement wave function is simply

$$\psi'(x, y) = \begin{cases} \frac{1}{\epsilon}, & \begin{aligned} & x \in [x_o - \epsilon/2, x_o + \epsilon/2] \\ & y \in [y_o - \epsilon/2, y_o + \epsilon/2], \end{aligned} \\ 0, & otherwise. \end{cases} \tag{4.80}$$

giving rise to the probability density $p_x(x, y)$ of Eq. (4.64). The probability density $p_p(p_x, p_y)$ of Eq. (4.65) follows immediately as the squared absolute value of the Fourier transformed wave function

$$\tilde{\psi}(k_x, k_y) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, e^{ixk_x} e^{iyk_y} \psi(x, y). \tag{4.81}$$

Before closing, it is interesting to note one final relation between the $\hat{x}$ and $\hat{p}$ operators. In the main text, we showed that operators can have simultaneous eigenvectors only if they commute. What is the commutator of the $\hat{x}$ and $\hat{p}$ operators? If $f(x)$ is any function in L^2, then we have

$$\hat{p}\hat{x} f(x) = -i\hbar \frac{d}{dx} x f(x) = -i\hbar f(x) - i\hbar f \frac{d}{dx} f(x) = (-i\hbar + \hat{x}\hat{p}) f(x) \tag{4.82}$$

so

$$[\hat{x}, \hat{p}] = i\hbar. \tag{4.83}$$

In fact, our order of presentation is somewhat inverted. In an empirical development of quantum mechanics, this *canonical commutation relation* is generally inferred from the classical mechanics of position and momentum and used to define the $\hat{x}$ and $\hat{p}$ operators.

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[a]The definition of the error here is intentionally vague. A precise statement is difficult. It should be clear, however, that the error referred to here deals with the intrinsic physical interaction between the measuring device and the system, not to external error such as mis-calibration or insensitive readout.

4.1.7   The Sixth Postulate: Quantum Dynamics

In the absence of outside perturbation, the wave vector of the system evolves according to the differential equation

$$i\hbar \frac{d}{dt} \psi(t) = \hat{H}\psi(t), \tag{4.84}$$

where $\hat{H}$ is the Hamiltonian operator for the system, corresponding to the total energy observable.

Our previous postulates have focused on the information that the state vector ψ provides us on the state of the system at a given instant in time. Real systems, however, are rarely static. Our final postulate allows us to predict the evolution of the state vector - and thus the physical characteristics of the system - as a function of time.

The Time-Dependent Schrödinger Equation

At the core of our six postulate lies the linear, first-order differential equation (4.84), commonly known as the *Time-Dependent Schrödinger Equation* after the Austrian physicist

Erwin Schrödinger who first recognized it significance. Despite its mathematical simplicity, the solution of this equation is in general highly nontrivial and will occupy much of the focus of the next section. At present, we restrict ourselves to some cursory observations on the mathematical and physical implications of the equation, noting only the simplest possible solutions.

At the start, a few key mathematical features are worth noting. First, let us clarify what is meant by the notation $\psi(t)$. Strictly speaking $\psi(t)$ represents a continuous, one-parameter sequence of state vectors, each of which is a member of the abstract Hilbert space $\mathcal{H}$ and represents the state of our physical system at a particular time. This continuity in the parameter t allows us to impose the typical framework of single-variable calculus on the vector-valued function $\psi(t)$: limits, integrals, and the time derivative of Eq. (4.84). The derivative, in particular, is defined by the limit[13]

$$\frac{d}{dt}\psi(t) = \lim_{\epsilon \to 0} \frac{\psi(t+\epsilon) - \psi(t)}{\epsilon}. \tag{4.86}$$

Note that by this definition and Eq. (4.84), the state vector $\psi(t)$ is necessarily continuous in time, i.e. can undergo no instantaneous jumps in value. Moreover, the normalization of the state vector is conserved:

$$\frac{d}{dt}\|\psi(t)\|^2 = \frac{d}{dt}(\psi(t), \psi(t)) = \left(\frac{d}{dt}\psi(t), \psi(t)\right) + \left(\psi(t), \frac{d}{dt}\psi(t)\right)$$
$$= \frac{i}{\hbar}\left(\hat{H}\psi(t), \psi(t)\right) - \frac{i}{\hbar}\left(\psi(t), \hat{H}\psi(t)\right) = 0, \tag{4.87}$$

where in the last equality we have relied on on the Hermitian property of the Hamiltonian $\hat{H}$.[14]

With these mathematical observations in hand, let us note some physical consequences. First, note that the time evolution of the system is entirely deterministic. Nondeterministic, random behavior appears only when external measurements are performed on the system. Second, the continuity of the state vector in time implies that in quantum mechanics physical observables always change smoothly in time, i.e. never through instantaneous jumps in value. Third, the conservation of the norm ensures that if $\psi(0)$ is a valid state vector, then $\psi(t)$ remains a valid state vector for all time. And, finally, because the differential equation Eq. (4.84) is linear in the state vector $\psi(t)$, the superposition principle we noted earlier is unaffected by time propagation. In other words, if $\psi(0)$ can be decomposed as

$$\psi(0) = \sum_n c_n \phi_n, \tag{4.88}$$

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[13]As usual, a sequence of vectors f_n in $\mathcal{H}$ is said to converge to a limit vector f if

$$\lim_{n \to \infty} \|f_n - f\| = 0. \tag{4.85}$$

A vector-valued function $\psi(t)$ is said to converge to the limit ψ_o as $t \to t_o$ if $\psi(t_n) \to \psi_o$ whenever $t_n \to t_o$.

[14]Our use of the "product rule" for the inner product in evaluating the time derivative is nontrivial but is readily obtained from the definition of the derivative in Eq. (4.86).

then for all t, we have

$$\psi(0) = \sum_n c_n \phi_n(t) \tag{4.89}$$

where $\phi_n(t)$ is the solution to Eq. (4.84) with ϕ_n as the initial condition at $t = 0$.

Time Evolution under a Static Hamiltonian

This superposition principle is particularly useful in analyzing systems where the Hamiltonian operator $\hat{H}$ is static in time. For note what happens if $\psi(0)$ is an eigenvector of $\hat{H}$ with some eigenvalue ε. In this case, it is easily verified that

$$\psi(t) = e^{-\frac{i}{\hbar}\varepsilon t}\psi(0) \tag{4.90}$$

is the unique solution to the time-dependent Schrödinger equation. Moreover, since the eigenvectors ϕ_n of $\hat{H}$ for a complete, orthonormal basis for any initial vector $\psi(0)$, the solution to Eq. (4.84) for a time-independent Hamiltonian $\hat{H}$ can always be written

$$\psi(t) = \sum_n e^{-\frac{i}{\hbar}\varepsilon_n t}\phi_n(\phi_n, \psi(0)) \tag{4.91}$$

where ε_n are the corresponding eigenvalues. Thus, if the eigenvectors and eigenvalues of the static Hamiltonian $\hat{H}$ are known, the time evolution of the system is completely determined. For this reason the eigenvalue equation

$$\hat{H}\psi = \epsilon\psi, \tag{4.92}$$

often referred to as the *Time Independent Schrödinger Equation*, is of critical importance in evaluating the behavior of quantum systems.

In general, however, the Hamiltonian operator $\hat{H}$ may not be static in time. Although Eq. (4.84) remains valid in this case, the solution of the equation is far more difficult and constitutes a field of study in its own right. This topic will be explored in more detail in the remainder of this chapter. First, however, we introduce several additional tools for dealing with quantum ensembles.

4.2   Dynamics of Quantum Ensembles

4.2.1   The Density Matrix

At the outset, we must be clear about two types of randomness that we will encounter in our analysis. In quantum mechanics, we often discuss the "quantum" randomness associated with making a measurement on a system with a particular wavefunction ψ: even though we may know the wavefunction, we cannot predict with certainty the result of measuring the

value of an arbitrary observable A. The most we can do is to predict ensemble quantities such as the expectation value of A – that is, the average value which would be obtained if the measurement were repeated infinitely many times on replicas of the same system *with identical wavefunctions before the measurement*. The key point here is that this type of randomness is an inherently quantum phenomenon with uncertainty determined *by* the wavefunction, even in the absence of uncertainty *in* the wavefunction.

In contrast, in classical statistical mechanics, we are used to thinking in terms of randomness introduced by uncertainty in our knowledge of the state of the system before the measurement. In classical mechanics, if we have sufficient knowledge of the state of our system (e.g. the position and momenta of all particles), the outcome of any measurement is completely determined already. However, when we work with large systems of many particles, we often know only bulk properties of the system or, equivalently, probability distributions for the properties of individual particles. For example, if we measure of the energy of a very large number of individual particles from a gas with temperature T, we know that we will get an *average* value of $k_b T$. However, we do not know beforehand what the result of any individual measurement will be. This type of randomness is fundammentally different from the quantum uncertainty discussed above: one is caused by a simple lack of knowledge about the system, while the other is due to an inherent limitation on the amount of information which *can* be known about the system.

In bulk measurements on quantum systems, both types of uncertainty are present. Just as for a single particle the expecation value of an observable A is obtained as

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle, \tag{4.93}$$

the expectation value of A in a system of of N particles is obtained by summing the contribution of each individual particle as

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle \psi_i | \hat{A} | \psi_i \rangle \tag{4.94}$$

where ψ_i is the wavefunction of the ith particle.[15]

Note that in this case, the sum extends over the number of particles in the system. If we instead know that the wavefunction of each particle in the system is chosen from a discrete (but not necessarily finite) set of wavefunctions $\{|\chi_1\rangle, |\chi_2\rangle, ...\}$, we can write the expectation value instead as

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^{\infty} n_i \langle \chi_i | \hat{A} | \chi_i \rangle. \tag{4.95}$$

where n_i is the number of particles with wavefunction $|\chi_i\rangle$ (note that $\sum_{i=0}^{\infty} n_i = N$). In another notation, we can define $p_i = \frac{n_i}{N}$ (so that $\sum_{i=0}^{\infty} p_i = 1$) and give the expectation value

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[15]We are implicitly assuming here that the particles do not interact: otherwise, it would be meaningless to speak of a wavefunction for one particle or another; only the composite wavefunction would be meaningful.

as

$$\langle A \rangle = \sum_{i=1}^{\infty} p_i \langle \chi_i | \hat{A} | \chi_i \rangle. \tag{4.96}$$

In the limit that $N \to \infty$, we can speak of these coefficients p_i as the probabilities for a randomly selected molecule to be in the $|\chi_i\rangle$ state. It should be emphasized that there need be nothing special about the wavefunctions $|\chi_i\rangle$ (in particular, they need not be orthonormal or complete); all we require is that whatever wavefunction a given particle might have be included in the set of $|\chi_i\rangle$'s.

Let's suppose that we have an orthonormal basis $|n\rangle$ for our Hilbert space, so that we can re-write the expectation value as

$$\begin{aligned} \langle A \rangle &= \sum_{i=1}^{\infty} p_i \langle \chi_i | \left(\sum_{n=1}^{\infty} |n\rangle \langle n| \right) \hat{A} | \chi_i \rangle \\ &= \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} p_i \langle \chi_i | n \rangle \langle n| \hat{A} | \chi_i \rangle \end{aligned} \tag{4.97}$$

Remember that the two inner products inside of the sum are just numbers, so we can change the order in any way we want. Switching the order and bringing the terms which depend only on n outside of the sum over i, we get

$$\begin{aligned} \langle A \rangle &= \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} p_i \langle n| \hat{A} | \chi_i \rangle \langle \chi_i | n \rangle \\ &= \sum_{n=1}^{\infty} \langle n| \hat{A} \left(\sum_{i=1}^{\infty} p_i | \chi_i \rangle \langle \chi_i | \right) |n\rangle \end{aligned} \tag{4.98}$$

The quantity inside the parentheses is an operator: it is in fact a sum over the projection operators $|\chi_i\rangle \langle \chi_i|$ weighted by the probability of observing the corresponding state. Defining this to be a new operator

$$\hat{\rho} \equiv \sum_{i=1}^{\infty} p_i | \chi_i \rangle \langle \chi_i |, \tag{4.99}$$

our sum becomes

$$\langle A \rangle = \sum_{n} \langle n| \hat{A}\hat{\rho} |n\rangle \equiv Tr\{\hat{A}\hat{\rho}\} \tag{4.100}$$

where in the last equality we have defined the *trace* of an operator as the sum of its diagonal matrix elements.

Effectively, all we have done here is to re-cast the expectation value of our observable *A* from a form involving wavefunctions to an expression which looks like the trace of the product of two matrices. However, the new operator $\hat{\rho}$, called the *density matrix* for our system, turns out to have many very convenient properties. First, since we can use $\hat{\rho}$ to determine the expectation value of arbitrary observables, it effectively serves as a complete replacement for our usual representation of the system in terms of wavefunctions. Indeed, this would be the case even if we had only one wavefunction for a single particle ψ to consider. In this case the density matrix would be simply

$$\hat{\rho} = |\psi\rangle \langle\psi|$$

and expectation values are obtained simply as

$$\langle A \rangle = \sum_n \langle n| \hat{A} \hat{\rho} |n\rangle = \sum_n \langle n| \hat{A} |\psi\rangle \langle\psi| n\rangle = \sum_n \langle\psi| n\rangle \langle n| \hat{A} |\psi\rangle = \langle\psi| \hat{A} |\psi\rangle \,.$$

Just as importantly, we will see below that, given an initial density matrix $\hat{\rho}(t_o)$ for our system, equations of motion for the time evolution of $\hat{\rho}$ are easily obtained and are directly analgous to the Schrodinger equation for the time evolution of a wavefunction. Indeed, it is this fact which allows us to examine the time-dependence of expectation values for the system solely in terms of the density matrix without explicitly considering wavefunctions at all. Finally, since calculating expectation values via the trace of an operator against $\hat{\rho}$ takes into account both the quantum statistics of the wavefunction *and* the ensemble statistics of the probabilities for the occupation of various states, density matrix calculations are tremendously useful for dealing with ensembles of (non-interacting) particles. In fact, in many cases – particularly for systems which begin in an equilibrium of some sort – we will find that time-dependnet calculations simplify significantly due to symmetries in the density matrix (namely, that off-diagonal entries are zero for equilibrium systems). But this is getting ahead of ourselves. In the following sections, we will begin by deriving an equation – the *Liouville Equation* – for the time-dependence of the density matrix analogous to the Schrödinger Equation for the wavefunction. We will then explore in some detail different representations of the time-evolution of our system, showing which representations may be useful in different contexts and ultimately introducing a perturbative expansion which describes the response of a well-behaved system to a (possibly not well-behaved) perturbation.

4.2.2 The Quantum Liouville Equation

Our first task is to find an expression for the time-evolution of the density matrix. The central question we want to answer is: if at time t_o the density matrix is $\hat{\rho}_o$, what is the density matrix $\hat{\rho}(t)$ at some later time t? The basis for our derivation is that, although we don't yet know anything about how $\hat{\rho}$ evolves in time, we do know that the wavefunctions $\hat{\chi}_i$ which compose it evolve according to the time-dependent Schrödinger equation (TDSE)

$$i\hbar \frac{d}{dt} |\chi\rangle = \hat{H} |\chi\rangle . \tag{4.101}$$

Proceeding quite informally, we can simply take the derivative of $\hat{\rho}$ with respect to time to obtain

$$
\begin{aligned}
\frac{d}{dt}\hat{\rho} &= \sum_{j=1}^{\infty} \frac{d}{dt} |\chi_j\rangle \langle \chi_j| = \sum_{j=1}^{\infty} \left\{ \left[\frac{d}{dt} |\chi_j\rangle \right] \langle \chi_j| + |\chi_j\rangle \left[\frac{d}{dt} \langle \chi_j| \right] \right\} \\
&= \sum_{j=1}^{\infty} \left\{ \frac{1}{i\hbar} \hat{H} |\chi_j\rangle \langle \chi_j| - \frac{1}{i\hbar} |\chi_j\rangle \langle \chi_j| \hat{H} \right\} \\
&= \frac{1}{i\hbar} \sum_{j=1}^{\infty} \left[\hat{H}, |\chi_j\rangle \langle \chi_j| \right] = \frac{1}{i\hbar} \left[\hat{H}, \hat{\rho} \right]
\end{aligned}
\tag{4.102}
$$

In the first equality, we have used a "product rule" to split up the derivative of the outer product into two separate terms, just as for the derivative of a product of two functions $f(t)$ and $g(t)$, we would use

$$\frac{d}{dt} f(t)g(t) = g(t)\frac{df(t)}{dt} + f(t)\frac{dg(t)}{dt}. \tag{4.103}$$

In the second line, we then used the TDSE (Eq. 4.101) to replace the derivatives in each term with the Hamiltonian acting on the projection operator from either the right or left. Finally, in the last line we simply recognized the expression as the commutator of the Hamiltonian with the density matrix.

This heuristic derivation has a number of subtleties which, to a reader encountering them for the first time, may – and in fact should – be somewhat troubling. The next sections will focus on a more detailed derivation of Eq. (4.102) and on the basic features of the time-evolution of $\hat{\rho}$ under various conditions.

The first to be addressed, perhaps, should be the very concept of taking the derivative of an operator. Intuitively, this should seem a reasonable prospect, but formally it may be somewhat difficult to grasp. Fortunately, the formal definition is straightforward: we say that the derivative of an operator $\hat{A}(t)$ is *defined* by examining the action of the operator on an arbitrary vector (wavefunction) $|\phi\rangle$. This is perhaps the most intuitive definition anyway: since an operator can be completely defined in terms of its action on a sufficiently large set of vectors (e.g. an orthonormal basis), it is natural that we should define the derivative in terms of the action of the "derived" operator on arbitrary vectors. More precisely, given a time-dependent operator $\hat{A}(t)$, we say that another operator $\hat{B}(t)$ is the derivative of $\hat{A}(t)$, i.e.

$$\frac{d}{dt} \hat{A}(t) = \hat{B}(t) \tag{4.104}$$

if (and only if) for *any* time-independent vector $|\phi\rangle$ in the domain of $\hat{A}$ it is true that

$$\frac{d}{dt}\left(\hat{A}(t)\,|\phi\rangle\right) = \hat{B}(t)\,|\phi\rangle. \tag{4.105}$$

In this last expression, we no longer take derivatives of operators, but instead simple derivatives of the time-dependent vector $\hat{A}(t)\,|\phi\rangle$, a procedure which is already well-defined in terms of basic calculus.

This definition gives a precise meaning to the first equality in the derivation of Eq. 4.102, but leaves some important questions unanswered with regard to the second equality: in particular, how are we justified in introducing the "chain rule" for splitting up the operator $|\psi_j\rangle\langle\psi_j|$? The proof is again not difficult, but rests on a clear understanding of what the terms we are using mean, particularly the braket notation symbols $|\psi\rangle$ and $\langle\psi|$. We often prefer to think of these terms as denoting, respectively, a complex function $\psi(\vec{r})$ and its complex conjugate $\psi^*(\vec{r})$. However, this is not quite correct: it is indeed true that $|\psi\rangle$ represents a complex function (or vector) $\psi(\vec{r})$ on a Hilbert space $\mathscr{H}$ consisting of all square-integrable functions of the coordinates $\vec{r}$; the bra, however, does not represent a simple complex conjugate, but rather a *linear functional* $F_\psi : \mathscr{H} \to \mathbb{C}$ which maps vectors ϕ from $\mathscr{H}$ onto the complex numbers $\mathbb{C}$ via the relation

$$\langle\psi|\,\phi\rangle = F_\psi\phi = \int d\tau\,\psi^*(\vec{r})\phi(\vec{r}) \tag{4.106}$$

in which the notation $d\tau$ indicates integration over the entire space. With this notation clear, it is easy to see that $|\psi\rangle\langle\psi|$ represents an operator on $\mathscr{H}$ since, given an arbitrary vector ϕ in $\mathscr{H}$, it returns the vector

$$|\psi\rangle\langle\psi|\,\phi\rangle = \psi(\vec{r})F_\psi\phi(\vec{r}) = \psi(\vec{r})\int d\tau\,\psi^*(\vec{r})\phi(\vec{r}) \tag{4.107}$$

which is simply the vector $\psi(\vec{r})$ scaled by the complex number $\langle\psi|\,\phi\rangle$. Likewise, for an arbitrary (time-independent) vector $|\phi\rangle$ we see that we can expand the derivative of *the action of this operator on* $|\phi\rangle$ as

$$\begin{aligned}
\frac{d}{dt}\,|\psi(t)\rangle\langle\psi(t)|\,\phi\rangle &= \frac{d}{dt}\left[\psi(\vec{r},t)\int d\tau\,\psi^*(\vec{r},t)\phi(\vec{r})\right]\\[6pt]
&= \left[\frac{d}{dt}\psi(\vec{r},t)\right]\int d\tau\,\psi^*(\vec{r},t)\phi(\vec{r}) + \psi(\vec{r},t)\left[\frac{d}{dt}\int d\tau\,\psi^*(\vec{r},t)\phi(\vec{r})\right]\\[6pt]
&= \left[\frac{d}{dt}\,|\psi\rangle\right]\langle\psi|\,\phi\rangle + |\psi\rangle\left[\frac{d}{dt}\,\langle\psi|\,\phi\rangle\right]
\end{aligned} \tag{4.108}$$

The first term here is just the time-derivative of $|\psi\rangle$ multiplied by a constant, while the second is the vector $|\psi\rangle$ multiplied by the time-derivative of the constant $\langle\psi|\,\phi\rangle$. To give a precise meaning to this expression in terms of the derivative of the bra functional, we note that just as we defined the time-derivative of an operator in terms of the action of the

"derived" operator on an arbitrary ket, the time-derivative of the linear functional $\langle \psi |$ is defined in terms of its action on an arbitrary ket $|\phi\rangle$, In other words, we *define* that a linear functional $G : \mathscr{H} \to \mathbb{C}$ is the derivative of another functional $F : \mathscr{H} \to \mathbb{C}$ if and only if

$$\frac{d}{dt}\left(F|\phi\rangle\right) = G|\phi\rangle \tag{4.109}$$

for any vector $|\phi\rangle$ in the domain of F. From this definition, it follows immediately that

$$\frac{d}{dt}|\psi(t)\rangle\langle\psi(t)|\,\phi\rangle = \left\{\left[\frac{d}{dt}[|\psi\rangle\right]\langle\psi| + |\psi\rangle\left[\frac{d}{dt}\langle\psi|\right]\right\}|\phi\rangle$$

or, since in Eq. 4.108 the vector $|\phi\rangle$ can be any vector in $\mathscr{H}$,

$$\frac{d}{dt}|\psi(t)\rangle\langle\psi(t)| = \left\{\left[\frac{d}{dt}[|\psi\rangle\right]\langle\psi| + |\psi\rangle\left[\frac{d}{dt}\langle\psi|\right]\right\}. \tag{4.110}$$

This brings us up through the second equality of Eq. 4.102. The remaining formality before obtaining our final expression is the second half of third equality, i.e. the statement that

$$|\psi\rangle\left[\frac{d}{dt}\langle\psi|\right] = -\frac{1}{i\hbar}|\psi\rangle\langle\psi|\hat{H}$$

Again, now that we have formal definitions in place, actually evaluating the equality is straightforward, making use of the TDSE (Eq. 4.101):

$$\begin{aligned}
|\psi\rangle\left[\frac{d}{dt}\langle\psi|\right] &= \psi(\vec{r},t)\int d\tau\phi(\vec{r})\left[\frac{d}{dt}\psi(\vec{r},t)\right]^* \\
&= \psi(\vec{r},t)\int d\tau\phi(\vec{r})\left[\frac{1}{i\hbar}\hat{H}\psi(\vec{r},t)\right]^* \\
&= -\frac{1}{i\hbar}|\psi\rangle\left\langle\left(\hat{H}\psi\right)\middle|\phi\right\rangle
\end{aligned} \tag{4.111}$$

Finally, we make use of the fact that $\hat{H}$ is Hermitian, i.e. $\hat{H} = \hat{H}^\dagger$ where the *adjoint* operator $\hat{H}^\dagger$ is defined by the property that for any two vectors $|\phi\rangle$ and $|\psi\rangle$

$$\left\langle\left(\hat{H}\psi\right)\middle|\phi\right\rangle \equiv \left\langle(\psi)\middle|\left(\hat{H}^\dagger\phi\right)\right\rangle. \tag{4.112}$$

It is because of this Hermitian property of $\hat{H}$ that we can write expressions like

$$\langle\psi|\hat{H}|\phi\rangle \tag{4.113}$$

without bothering about whether $\hat{H}$ "acts" to the right or left in the braket notation. In the case of Eq. 4.111, this notation means that we can write without ambiguity

$$|\psi\rangle \left[\frac{d}{dt} \langle\psi| \right] = -\frac{1}{i\hbar} |\psi\rangle \langle\psi| \hat{H} |\phi\rangle . \qquad (4.114)$$

Taking everything together, we have in the end a somewhat more rigorous derivation of Eq. 4.102 above:

$$\frac{d}{dt}\hat{\rho} = \frac{1}{i\hbar} \left[\hat{H}, \hat{\rho} \right] \qquad (4.115)$$

This is the much-celebrated Liouville Equation (or *Liouville-Von Neumann Equation*), which governs the time-evolution of the density matrix operator $\hat{\rho}$. With this expression, we can begin to think of taking time-dependent expectation values via

$$\langle A(t) \rangle = Tr\{\hat{A}\hat{\rho}(t)\} \qquad (4.116)$$

where $\hat{\rho}(t)$ is the solution to Eq. 4.115. In the next several sections, we will first examine the specific solutions to the Liouville equation which occur when $\hat{H}$ is time-independent and then obtain a series expansion for $\hat{\rho}(t)$ under the action of an arbitrary time-dependent perturbation.

4.2.3   Evolution under a Static Hamiltonian

Just as for wavefunctions, the simplest type of evolution to deal with in the Liouville equation is when the Hamiltonian $\hat{H}$ is time-independent. In this case, it becomes convenient to expand the density matrix in terms of an orthonormal basis of eigenfunctions of $\hat{H}$:[16]

$$\hat{\rho} = \sum_{m,n=1}^{\infty} |m\rangle \langle m| \hat{\rho} |n\rangle \langle n| \equiv \sum_{m,n=1}^{\infty} \rho_{mn} |m\rangle \langle n| . \qquad (4.117)$$

Taking the *mn* matrix element of both sides of Eq. 4.115, we obtain

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[16]In what follows, we will treat $\hat{H}$ as though it posesses a discrete spectrum of eigenvalues. Though this may not generally be the case, the manipulations are significantly easier in this case, and the framework is not fundamentally changed. In the case of a Hamiltonian with a continuous spectrum of eigenvalues, terms such as the sum over eigenvector projection operators should be replaced with integrals over the eigenvalue spectrum with a family of spectral projection operators for $\hat{H}$. Note also that for the Hilbert spaces we work with (square integrable complex functions of some *n*-dimensional coordinate vector), although the dimensionality of the space is infinite, it is nonetheless countable, i.e. the space always contains a countable dense set, allowing for a *countable* (though infinite) orthonormal basis. For more details, see Jordan or Stone.

$$\frac{d}{dt}\rho_{mn} = \langle m| \frac{d}{dt}\hat{\rho} |n\rangle$$

$$= \frac{1}{i\hbar} \langle m| \left[\hat{H}\hat{\rho} - \hat{\rho}\hat{H}\right] |n\rangle$$

$$= \frac{E_m - E_n}{i\hbar}\rho_{mn} \tag{4.118}$$

This is a simple separable differential equation for the *number* ρ_{mn}, which gives

$$\rho_{mn} = \exp\left(\frac{E_{mn}}{i\hbar}(t - t_o)\right)\rho_{mn}(t_o). \tag{4.119}$$

Several points are worth stopping to take note of here. First, notice that in this expression, the diagonal elements of $\hat{\rho}(t)$ are constant in time, i.e. for a static Hamiltonian

$$\rho_{mn}(t) = \rho_{mn}(t_o) \tag{4.120}$$

The off-diagonal elements, in contrast, oscillate in time with a frequency of $\frac{E_{mn}}{\hbar}$. It is these oscillating off-diagonal elements which give rise to the time-dependence of the expectation values of various observables. In particular, if an operator $\hat{A}$ commutes with $\hat{H}$, then in the eigenbasis of $\hat{H}$, its matrix representation will be diagonal so that the time-dependent expectation value becomes

$$\langle A \rangle = \sum_{m,n=0}^{\infty} \langle m| \hat{A} |n\rangle \langle n| \hat{\rho} |m\rangle = \sum_{m=0}^{\infty} A_{mm}\rho_{mm}(t_o) \tag{4.121}$$

In this case, the expectation value is seen to be *independent of time*, and we say that the observable A is a *constant of the motion*. In contrast, if $\hat{A}$ does not commute with $\hat{H}$ (i.e. is not diagonal in the $\hat{H}$ eigenbasis), we have

$$\langle A \rangle = \sum_{m,n=0}^{\infty} A_{mn}\rho_{nm} = \sum_{m,n=0}^{\infty} A_{mn} \exp\left(\frac{E_{mn}}{i\hbar}(t - t_o)\right)\rho_{mn}(t_o)$$

$$= \sum_{m=0}^{\infty} A_{mm}\rho_{mm}(t_o) + \sum_{m<n} A_{mn} \exp\left(\frac{E_{mn}}{i\hbar}(t - t_o)\right)\rho_{mn}(t_o)$$

$$+ \sum_{m>n} A_{mn} \exp\left(\frac{E_{mn}}{i\hbar}(t - t_o)\right)\rho_{mn}(t_o)$$

$$= \sum_{m=0}^{\infty} A_{mm}\rho_{mm}(t_o) + 2\Re \sum_{m<n} A_{mn} \exp\left(\frac{E_{mn}}{i\hbar}(t - t_o)\right)\rho_{mn}(t_o) \tag{4.122}$$

In the last step we have noted that since both $\hat{A}$ and $\hat{\rho}(t_o)$ are Hermitian, we have $A_{mn} = A_{nm}^*$ and $\rho_{mn} = \rho_{nm}^*$. If we write these matrix elements as a product of a real number with a complex phase, i.e.

$$A_{mn}\rho_{mn}(t_o) = a_{mn}e^{ib_{mn}} \tag{4.123}$$

we can re-write this expression as

$$
\begin{aligned}
\langle A \rangle &= \sum_{m=0}^{\infty} A_{mm}\rho_{mm}(t_o) + 2 \sum_{m<n} a_{mn}\mathfrak{R} \exp\left(ib_{mn} - i\frac{E_{mn}}{\hbar}(t - t_o)\right) \\
&= \langle A \rangle_{t_o} + 2 \sum_{m<n} a_{mn} cos\left(b_{mn} - \omega_{mn}(t - t_o)\right)
\end{aligned} \tag{4.124}
$$

where $\omega_{mn} \equiv \frac{E_{mn}}{\hbar}$. In this case, we can see that the expectation value of A will oscillate around the t_o value with the oscillations consisting of a sum of (infinitely many) cosine terms with frequency ω_{mn}. It also becomes clear in this case that the magnitude of the off-diagonal elements in ρ_{mn} – expressed in the eigenbasis of the Hamiltonian – will determine the strength of the oscillations. In particular, if $\hat{\rho}(t_o)$ commutes with $\hat{H}$ (i.e. is diagonal in the $\hat{H}$ eigenbasis), the expectation value of *all observables* will be constant in time. Actually, we could see this directly from the Liouville equation without any further manipulations: since the time-derivative of $\hat{\rho}$ is proportional to the commutator of $\hat{\rho}$ with $\hat{H}$, it is clear that if the two commute, the density matrix (and hence all bulk observables) cannot evolve in time. This observation suggests something that we will see in more detail shortly: for a system in equilibrium under a time-constant Hamiltonian, the density matrix is diagonal in the eigenbasis of the Hamiltonian.

4.2.4 The Dyson Expansion

Finally, we turn to the general case of a time-varying Hamiltonian. Although solving the Liouville equation in general will of course depends on the particular characteristics of the Hamiltonian of the system–and is not in general possible analytically–what we will do here is to develop a perturbative expansion in time in which successive orders of the perturbation are necessary for longer time intervals away from t_o. To do this we begin with Eq. (4.115) and note that if we integrate[17] both sides we obtain

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[17]The reader may be getting tired of formal definitions by this point, but it is nonetheless worth pointing out that formally the integral of an operator can be defined just as the derivative was: in terms of the action of the "integrated" operator on an arbitrary vector. Given an operator $\hat{A}(t)$ we say that the operator $\hat{B}(t)$ is the integral of $\hat{A}$ from t_o to t if for any time-independent vector $|\phi\rangle$ in the domain of $\hat{A}$ it holds that

$$\hat{B}(t)|\phi\rangle = \int_{t_o}^{t} dt_1 \hat{A}(t_1)|\phi\rangle \tag{4.125}$$

Just as above, the more abstract quantity (the operator integral) is defined in terms of the more familiar integral of the time-dependent vector $\hat{A}(t_1)|\phi\rangle$.

$$\hat{\rho} = \hat{\rho}(t_o) + \frac{1}{i\hbar} \int_{t_o}^{t} dt_1 \left[\hat{H}(t_1), \hat{\rho}(t_1)\right] \tag{4.126}$$

Now comes the all-important step: we substitute this expression for $\hat{\rho}$ into itself to obtain a second equation (really just a re-statement of the first) which reads

$$\hat{\rho} = \hat{\rho}(t_o) + \frac{1}{i\hbar} \int_{t_o}^{t} dt_1 \left[\hat{H}(t_1), \hat{\rho}(t_o) + \frac{1}{i\hbar} \int_{t_o}^{t_1} dt_2 \left[\hat{H}(t_2), \hat{\rho}(t_2)\right]\right]$$

$$= \hat{\rho}(t_o) + \frac{1}{i\hbar} \int_{t_o}^{t} dt_1 \left[\hat{H}(t_1), \hat{\rho}(t_o)\right] + \frac{1}{(i\hbar)^2} \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 \left[\hat{H}(t_1), \left[\hat{H}(t_2), \hat{\rho}(t_2)\right]\right]$$

Although it might not seem like much of an improvement at first, notice that in this last expression the first two terms depend only on $\hat{\rho}(t_o)$, not on $\hat{\rho}$ at any later time. Given $\hat{\rho}(t_o)$, these terms can be evaluated easily, leaving only the last term as an unknown. Moreover, we can repeat the process as many times as we like to obtain at N^{th} order

$$\hat{\rho} = \sum_{n=0}^{N-1} \frac{1}{(i\hbar)^n} \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 ... \int_{t_o}^{t_{n-1}} dt_n \left[\hat{H}(t_1), \left[\hat{H}(t_2), ..., [\hat{H}(t_n), \hat{\rho}(t_o)]\right]\right]$$

$$+ \frac{1}{(i\hbar)^N} \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 ... \int_{t_o}^{t_{N-1}} dt_N \left[\hat{H}(t_1), \left[\hat{H}(t_2), ..., [\hat{H}(t_N), \hat{\rho}(t_N)]\right]\right] . \tag{4.127}$$

This form suggests already that we take a limit as N approaches infinity, and obtain a closed form expression in terms of an infinite sum over nested commutators of $\hat{H}$ with $\hat{\rho}$, i.e.

$$\hat{\rho} = \sum_{n=0}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 ... \int_{t_o}^{t_{n-1}} dt_n \left[\hat{H}(t_1), \left[\hat{H}(t_2), ..., [\hat{H}(t_n), \hat{\rho}(t_o)]\right]\right] . \tag{4.128}$$

It may not be obvious, however, whether such a sum should be expected to converge: indeed, since each successive term involves a higher power of $\hat{H}$'s , it would seem that the convergence should depend on some "magnitude" of $\hat{H}$. We will not consider convergence issues in any detail here, but we will provide at least a hint at why the sum will often converge. Observe that each successive term in the sum involves an integral over successively higher dimensional volume; more importantly, each n-dimensional integral covers a successively smaller fraction of the n-dimensional cube of side length t. For example, the first integral covers a one-dimensional volume (i.e. length) of

$$\int_{0}^{t} dt_1 = t \tag{4.129}$$

(we have here set $t_o = 0$) The second integral covers the two-dimensional volume (i.e. area)

$$\int_0^t dt_1 \int_0^{t_1} dt_2 = \int_0^t dt_1 t_1 = \frac{t^2}{2} \tag{4.130}$$

More generally, we see that each added integral simply results in a higher power of t and a (factorially) larger denominator, i.e.

$$\int_0^t dt_1 \int_0^{t_1} dt_2 ... \int_0^{t_{n-1}} dt_n = \frac{t^n}{n!} \tag{4.131}$$

Of course we are not actually evaluating the "magnitude" of the nth term, only the integrated n-dimensional volume. Nonetheless, the decreasing volume of the region clearly limits in some sense the magnitude of the total integral; informally, we can think that, just as in the Taylor expansion for the exponential function, the presence of the $n!$ in the denominator should provide the necessary "suppression" of higher-order terms, ultimately causing the sum to converge. In fact, if the Hamiltonian were to commute with itself at all times (as in the previous subsection), this is precisely what the sum would reduce to: a simple exponential of a single one-dimensional integral over the Hamiltonian just as we found above.

Although this is by no means a rigorous proof, for our purposes here we will take it for granted that the sum (4.128) converges. Even so, for practical purposes, what we really want is to employ a truncated version of the expansion as an approximation for our density matrix. For example, we might truncate the sum at first order to obtain a linear approximation of the time-dependent density matrix:

$$\hat{\rho}(t_o) \approx \hat{\rho}(t_o) + \frac{1}{i\hbar} \int_{t_o}^t dt_1 \left[\hat{H}, \hat{\rho}(t_o) \right] . \tag{4.132}$$

Whether or not such an expansion is useful, however, does depend strongly on the "magnitude" of the Hamiltonian[18] relative to the timescale over which we wish to follow $\hat{\rho}$, just as for a Taylor expansion of a simple exponential $e^x = 1 + x^2 + \frac{x^3}{6} + ...$ the quality of the approximation $e^x \approx 1 + x$ depends strongly on the magnitude of x. In fact, for many situations, the sum (4.128) may converge very slowly, making it of little utility by itself as a means of approximating the time-evolution of $\hat{\rho}$.

As the reader may have guessed, however, there are cases where we can re-cast Eq. 4.128 into a form which does converge quickly so that approximating the sum by only a few terms gives a reasonable description of the dynamics of our system. One of the most important examples of such cases is for systems in which the Hamiltonian can be separated into two terms, one of which is time-independent (what we'll call the static Hamiltonian, $\hat{H}_o$) and the other of which is time-dependent (the perturbation, $\hat{V}(t)$). In this case, the quantum Liouville equation takes the form

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[18]Note that the units work out properly here: $\hat{\rho}$ is unitless, while $\hat{H}$ has units of energy. Since the integral likewise contributes units of time, the factor of $\hbar$ in the denominator provides the necessary units (energy by time) to make the overall term unitless.

$$\frac{d}{dt}\hat{\rho} = \frac{1}{i\hbar}\left[\hat{H}_o, \hat{\rho}\right] + \frac{1}{i\hbar}\left[\hat{V}(t), \hat{\rho}\right].$$
(4.133)

Notice that up until the addition of the final term on the right hand side, the expression looks like just the evolution of $\hat{\rho}$ under the static Hamiltonian $\hat{H}_o$, a result of the linearity of the commutator $\left[\hat{H}, \hat{\rho}\right]$. As we will explore in the next several sections, it is possible in this case to separate out the part of the dynamics which are due to the perturbing Hamiltonian from that part due to the static Hamiltonian (which can be solved exactly); we then use an expansion similar to Eq. 4.128 to add the effects of the perturbation into the system to some (generally low) order. For systems where the static portion of the Hamiltonian is large in magnitude compared to the perturbation, it will often be a quite reasonable approximation to truncate the expansion at first or second order, giving much simplified descriptions of the dynamics of our system than would be obtained otherwise. In fact this is precisely the approach adopted in spectroscopy: the static Hamiltonian $\hat{H}_o$ then represents the Hamiltonian of the isolated system which is then perturbed by a time-dependent potential $\hat{V}(t)$ in the form of an electromagnetic field. Expanding to first order in the field gives rise to effects such as "linear" absorption, while non-linear spectroscopies correspond to higher-order terms. In the next several sections, we develop this perturbative expansion and in then examine its application to spectroscopy.

4.3 The Time Evolution Operator

In order to develop this perturbative expansion simply and directly, it is convenient to introduce a slightly different representation of time evolution than we have used so far. To this point, we have based our analysis on a differential equation (Eq. (4.101), the TDSE) for a time-dependent *vector* $|\psi(t)\rangle$. By this point, we have introduced sufficiently sophisticated operator mechanics to be able to view the equation in a different light: in terms of a differential equation for a time-dependent *operator* $\hat{U}(t, t_o)$. Suppose we define a time-dependent operator $\hat{U}(t, t_o)$ by the property that

$$|\psi(t)\rangle = \hat{U}(t, t_o) |\psi(t_o)\rangle, \tag{4.134}$$

where $|\psi(t_o)\rangle$ is an arbitrary (normalized) ket at some starting time t_o, and $|\psi(t)\rangle$ is the ket to which $|\psi(t_o)\rangle$ would evolve, according to the Schrödinger equation, at some time $t > t_o$ (and similarly, for $t < t_o$, $\hat{U}(t, t_o)$ is the operator which maps $|\psi(t)\rangle$ to $|\psi(t_o)\rangle$). Let us be clear first that this is a precise definition: We know that introducing any normalized starting vector $|\psi(t_o)\rangle$ as an initial condition for the Schrödinger equation is enough to determine a unique time-dependent $|\psi(t)\rangle$ as a solution. What we do now is simply to define an operator (depending on t and t_o) which maps the starting vector to the final vector.

4.3.1 Basic Properties

Notice the following properties that must be satisfied by $\hat{U}(t, t_o)$:

1. **Identity at** $t = t_o$. When $t = t_o$, we must have $\hat{U}(t_o, t_o) = \hat{1}$ since the wave-function has not yet undergone any time evolution.

2. **Preservation of the Norm**. Since a wavefunction $|\psi(t)\rangle$ evolving under a Hermitian Hamiltonian $\hat{H}$ will always preserve its norm (i.e. $\langle\psi(t)| \psi(t)\rangle = \langle\psi(t_o)| \psi(t_o)\rangle$), it follows that the time-evolution assiciated with $\hat{U}(t, t_o) |\psi\rangle$ must likewise preserve the norm of the starting vector $|\psi\rangle$.

3. **Existence of an Inverse**. Clearly $\hat{U}(t, t_o)$ posesses an inverse operator $\hat{U}^{-1}(t, t_o)$ since for any vector $|\psi(t)\rangle$ in the range of $\hat{U}(t, t_o)$ there by definition exists a vector $|\psi(t_o)\rangle$ for which $|\psi(t)\rangle = \hat{U}(t, t_o) |\psi(t_o)\rangle$. As a result, we can simply define an operator $\hat{U}^{-1}(t, t_o)$ which maps all such vectors $|\psi(t)\rangle$ to the corresponding vector $|\psi(t_o)\rangle$.

4. **Unitarity**. Together with linearity, the two properties listed above (preservation of the norm and existence of an inverse) define what is called a *unitary* operator. Unitary operators are of special significance in quantum mechanics since they represent not only time evolution (as we have seen here for $\hat{U}(t, t_o)$) but also, as we will see later, basis set transformations and spatial rotations. We stop here to note only a few special properties of unitary operators which will be central to our work.

(a) *Preservation of Inner Products.* One special property of unitary operators is that, because they preserve the norm, they also preserve inner products, i.e. given two vectors $|\psi\rangle$ and $|\psi\rangle$, if we apply the unitary operator $\hat{U}$ to each vector, we find that $\langle \hat{U}\psi | \hat{U}\phi \rangle = \langle \psi | \phi \rangle$. To see this, define $|\chi\rangle = |\phi\rangle + |\psi\rangle$ and observe that

$$\|\hat{U}\chi\|^2 = \|\hat{U}\phi\|^2 + \|\hat{U}\psi\|^2 + 2\Re \langle \hat{U}\psi | \hat{U}\phi \rangle$$
$$\|\chi\|^2 = \|\phi\|^2 + \|\psi\|^2 + 2\Re \langle \hat{U}\psi | \hat{U}\phi \rangle$$

Because $\hat{U}$ is unitary, we know that $\|\hat{U}\chi\|^2 = \|\chi\|^2$, $\|\hat{U}\phi\|^2 = \|\phi\|^2$, and $\|\hat{U}\psi\|^2 = \|\psi\|^2$. Subtracting the two equations above, then, we must conclude that $\Re \langle \hat{U}\psi | \hat{U}\phi \rangle = \Re \langle \psi | \phi \rangle$. Similarly, by defining $|\chi\rangle = |\phi\rangle - |\psi\rangle$, we can show that $\Im \langle \hat{U}\psi | \hat{U}\phi \rangle = \Im \langle \psi | \phi \rangle$, so that in total we have as claimed

$$\langle \hat{U}\psi | \hat{U}\phi \rangle = \langle \psi | \phi \rangle. \tag{4.135}$$

(b) *Equivalence of the Adjoint and Inverse.* For an operator $\hat{U}$ to be unitary, it is required that it must posess an inverse. Furthermore, due to its norm-preserving property, it is also true that its adjoint operator is equal to this inverse. By definition of the adjoint, given two arbitrary vectors $|\psi\rangle$ and $|\phi\rangle$, we have

$$\langle \phi | \psi \rangle = \langle \hat{U}\phi | \hat{U}\psi \rangle = \langle \phi | \hat{U}^\dagger \hat{U}\psi \rangle \tag{4.136}$$

But this implies that $\hat{U}^\dagger \hat{U} = \hat{1}$ since $|\phi\rangle$ and $|\psi\rangle$ can be arbitrary vectors (in particular, $|\psi\rangle$ could be a basis vector, and clearly $\hat{U}^\dagger \hat{U} |\phi\rangle$ has the same representation in this basis as does $|\phi\rangle$). As a result, we have

$$\hat{U}^\dagger - \hat{U}^{-1} = \left(\hat{U}^\dagger - \hat{U}^{-1} \right) \hat{U}\hat{U}^{-1} = \left(\hat{U}^\dagger \hat{U} - \hat{U}^{-1}\hat{U} \right) \hat{U}^{-1} = \hat{0}$$

which is equivalent to

$$\hat{U}^\dagger = \hat{U}^{-1}. \tag{4.137}$$

In fact (though we do not stop to prove it here), this condition is reversible: a linear operator $\hat{U}$ is unitary *if an only if* it is true that $\hat{U}^\dagger \hat{U} = \hat{U}\hat{U}^\dagger = \hat{1}$.

4.3.2   Operator form of the Schrödinger Equation

Now that we know some general properties, of this unitary operator $\hat{U}(t, t_o)$, how do we find specifically what it is? The answer comes, as usual, from the TDSE. Using our definition

$|\psi(t)\rangle = \hat{U}(t, t_o) |\psi(t_o)\rangle$ and denoting the time-independent starting vector $|\psi(t_o)\rangle$ as simply $|\psi\rangle$ we have

$$i\hbar \frac{d}{dt} \left(\hat{U}(t, t_o) |\psi\rangle \right) = \hat{H} \left(\hat{U}(t, t_o) |\psi\rangle \right) \tag{4.138}$$

Now we begin again a familiar process: this equation holds for an arbitrary time-independent starting vector $|\psi\rangle$. As a result, by our definition of the derivative of an operator, this is entirely equivalent to the *operator* differential equation

$$i\hbar \frac{d}{dt} \hat{U}(t, t_o) = \hat{H} \hat{U}(t, t_o) \tag{4.139}$$

with the boundary condition $\hat{U}(t_o, t_o) = \hat{1}$. Equivalently, in integrated form, we have

$$\hat{U}(t, t_o) = \hat{1} + \frac{1}{i\hbar} \int_{t_o}^{t} dt_1 \hat{H}(t_1) \hat{U}(t_1, t_o). \tag{4.140}$$

As usual, both the derivative and integral should be thought of in terms of their action on an arbitrary time-independent starting vector $|\psi\rangle$.

Not surprisingly, while Eq. (4.139) is easy to write down, it is usually quite difficult to solve. Just as in the case of the wavefunction version of the TDSE, however, simple solutions do exist in the special case where the Hamiltonian $\hat{H}$ is either constant or commutes with itself at all times. For example, when $\hat{H}$ is static, Eq. (4.139) results in the *exponential* operator

$$\hat{U}(t, t_o) = e^{\frac{\hat{H}t}{i\hbar}} \tag{4.141}$$

defined in terms of either its operation on an arbitrary eigenvector $|n\rangle$ of $\hat{H}$

$$e^{\frac{\hat{H}t}{i\hbar}} |n\rangle = e^{\frac{E_n t}{i\hbar}} |n\rangle \tag{4.142}$$

or via a series expansion[19]

$$e^{\frac{\hat{H}t}{i\hbar}} = \sum_{n=0}^{\infty} \left(\frac{t}{i\hbar} \right)^n \frac{\hat{H}^n}{n!}. \tag{4.143}$$

---

[19] Although we will not stop to prove it here, both definitions are equivalent. In general, one should be careful to consider convergence when defining an operator expansion in this manner; in the present case, convergence is quite robust thanks to the factorially increasing denominator. As might be expected by this point, convergence of an operator series is defined in terms of the action of the truncated sum on an arbitrary vector. We say that the infinite operator sum

$$\sum_{n=0}^{\infty} \hat{A}_n \tag{4.144}$$

converges to a definite operator $\hat{A}$ if for an arbitrary vector $|\psi\rangle$ and an arbitrary positive number ε there exists an integer M such that for $N > M$

Note that by either definition $\hat{H}$ commutes with the exponential $e^{\frac{\hat{H}t}{i\hbar}}$. Since an arbitrary vector can be decomposed into an expansion over the eigenvector basis $|n\rangle$, to take the derivative of the exponential operator, we can examine the action of the operator on its eigenvector basis:

$$\frac{d}{dt}\left(e^{\frac{\hat{H}t}{i\hbar}}|n\rangle\right) = \frac{d}{dt}\left(e^{\frac{E_n t}{i\hbar}}|n\rangle\right) = \frac{E_n}{i\hbar}e^{\frac{E_n t}{i\hbar}}|n\rangle. \tag{4.146}$$

For an arbitrary vector $|\psi\rangle = \sum_n c_n |n\rangle$, we have then

$$
\begin{aligned}
\frac{d}{dt}\left(e^{\frac{\hat{H}t}{i\hbar}}|\psi\rangle\right) &= \frac{d}{dt}\left(\sum_n c_n e^{\frac{\hat{H}t}{i\hbar}}|n\rangle\right) \\
&= \sum_n c_n \frac{E_n}{i\hbar}e^{\frac{E_n t}{i\hbar}}|n\rangle \sum_n c_n \frac{\hat{H}}{i\hbar}e^{\frac{\hat{H}t}{i\hbar}}|n\rangle \\
&= \frac{\hat{H}}{i\hbar}e^{\frac{\hat{H}t}{i\hbar}}\left(\sum_n c_n |n\rangle\right) = \frac{\hat{H}}{i\hbar}e^{\frac{\hat{H}t}{i\hbar}}|\psi\rangle
\end{aligned}
\tag{4.147}
$$

or in other words

$$\frac{d}{dt}e^{\frac{\hat{H}t}{i\hbar}} = \frac{\hat{H}}{i\hbar}e^{\frac{\hat{H}t}{i\hbar}} \tag{4.148}$$

which is clearly a solution to the operator TDSE Eq. (4.139).

A similar result is obtained for the special case considered earlier where $\hat{H}$ is not time-constant, but has the special property that $\left[\hat{H}(t_2), \hat{H}(t_1)\right] = \hat{0}$ for all t_1 and t_2. Just as before, we note that in this case, since $\hat{H}$ commutes with itself at all times, we can always choose a time-independent basis which is composed of eigenvectors of $\hat{H}(t)$ at all times, although the eigenvalues $E_n(t)$ may vary. Consider the operator

$$\hat{U}(t, t_o) = e^{\frac{1}{i\hbar}\int_{t_o}^{t} dt_1 \hat{H}(t_1)} \tag{4.149}$$

where again we define the operator in terms of its action on the static eigenbasis of $\hat{H}(t)$ via

$$e^{\frac{1}{i\hbar}\int_{t_o}^{t} dt_1 \hat{H}(t_1)}|n\rangle = e^{\frac{1}{i\hbar}\int_{t_o}^{t} dt_1 \hat{E}_n(t_1)}|n\rangle. \tag{4.150}$$

Just as above, a short calculation verifies that taking the derivative of the operator applied to an eigenvector $|n\rangle$ returns simply $\frac{E_n(t)}{i\hbar}e^{\frac{1}{i\hbar}\int_{t_o}^{t} dt_1 \hat{E}_n(t_1)}$, and that as a result

$$\frac{d}{dt}e^{\frac{1}{i\hbar}\int_{t_o}^{t} dt_1 \hat{H}(t_1)} = \frac{\hat{H}}{i\hbar}e^{\frac{1}{i\hbar}\int_{t_o}^{t} dt_1 \hat{H}(t_1)} \tag{4.151}$$

$$\left\|\sum_{n=0}^{N}\hat{A}_n\psi - \hat{A}\psi\right\| < \epsilon\|\psi\|. \tag{4.145}$$

As usual, time-evolution under an arbitrary time-varying Hamiltonian is often very difficult (if not impossible) to solve analytically. However, just as we earlier obtained a series expansion for the density matrix under an arbitrary time-dependent Hamiltonian, we can obtain a series expansion for $\hat{U}(t, t_o)$ by repeatedly plugging Eq. (4.140) into itself to obtain the *Dyson series* expansion for the time-evolution operator

$$\hat{U}(t, t_o) = \sum_n \left(\frac{1}{i\hbar}\right)^n \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 ... \int_{t_o}^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2)...\hat{H}(t_n). \tag{4.152}$$

Just as in the case of the density matrix expansion described above, the convergence of this series is not necessarily expected to be quick, making it of limited utility for a truncated expansion. However, with the material just developed, we are finally ready to introduce a perturbative expansion which in many cases will converge quickly (just as discussed earlier in the context of the time-dependent density matrix), making a truncation of the sum after only a few terms a viable option. In the next section we develop this expansion for the time-evolution operator as an example and in the following section apply it to the density matrix representation.

4.3.3 Interaction Representation

The perturbative expansion we will develop here relies on a division of the system Hamiltonian into two terms: a static (time-independent) Hamiltonian $\hat{H}_o$ and a time-dependent (arbitrary) perturbation $\hat{V}(t)$ which may not bear any special relationship with $\hat{H}_o$ (in particular the two need not commute). Our approach will be to separate out the time-evolution of the system due to $\hat{H}_o$ (which can be solved exactly) from that due to $\hat{V}(t)$ (to which we will apply a series expansion). In this way, we fully account for the effects of the static Hamiltonian $\hat{H}_o$ on the system, while approximately accounting for the effects of the more difficult $\hat{V}(t)$.

The first step in this process is to introduce a *unitary transformation* on our Hilbert space. Mathematically, the meaning here is quite simple: a unitary transformation $\mathscr{U}$ is a one-to-one mapping $\mathscr{U} : \mathscr{H} \to \mathscr{H}$ from a Hilbert space $\mathscr{H}$ into itself which preserves inner products. Formally, $\mathscr{U}$ is a mapping which associates every vector $|\psi\rangle$ in $\mathscr{H}$ with another vector $\mathscr{U}(|\psi\rangle)$ in $\mathscr{H}$ such that

1. If $|\phi\rangle \neq |\psi\rangle$, then $\mathscr{U}(|\phi\rangle) \neq \mathscr{U}(|\psi\rangle)$, i.e. the mapping is *injective* (distinct elements $|\psi\rangle$ have distinct images under $\mathscr{U}$).

2. The set of image vectors $\{\mathscr{U}(|\psi\rangle)\}$ is equal to $\mathscr{H}$, i.e. the mapping is *surjective* or *onto*: every element in $\mathscr{H}$ is the image of another element of $\mathscr{H}$ under $\mathscr{U}$. Note that together with the previous requirement, this implies that the mapping $\mathscr{U}$ is *bijective* or *one-to-one*, i.e. both injective and surjective. In short, this property says that under $\mathscr{U}$ each vector in $\mathscr{H}$ is mapped to exactly one unique vector (also in $\mathscr{H}$), and that no

two distinct vectors are mapped to the same image vector. This likewise implies the existence of an inverse mapping $\mathscr{U}^{-1}$, which is also bijective, defined by the property that

$$\mathscr{U}^{-1}\left(\mathscr{U}\left(|\psi\rangle\right)\right) = |\psi\rangle . \tag{4.153}$$

3. For any two elements $|\phi\rangle$ and $|\psi\rangle$ in $\mathscr{H}$, it holds that $\langle\mathscr{U}(\psi)|\,\mathscr{U}(\phi)\rangle = \langle\psi|\,\phi\rangle$, i.e. the inner product between two vectors is the same as the inner product between their image vectors.

From these properties and our preceding discussion, it should be immediately clear[20] that a unitary operator $\hat{U}$ on a Hilbert space $\mathscr{H}$ defines a unitary transformation $\mathscr{U} : \mathscr{H} \to \mathscr{H}$ and vice-versa; the two are completely equivalent, and in the future we will not distinguish between them unless explicitly necessary. Actually, this is simply an example of the fact that any linear operator on a Hilbert space $\mathscr{H}$ corresponds by definition to a particular type of mapping (or transformation) of the vectors of some subset of $\mathscr{H}$ into another subset of $\mathscr{H}$, although the more general term "transformation" may refer to other types of mappings (e.g. non-linear mappings within a Hilbert space or mappings between two different Hilbert spaces).

Unitary transformations are important in physics for several reasons. Perhaps most fundamentally, it should be clear by now that physical time-evolution in quantum mechanics corresponds mathematically to a simple unitary transformation on the system Hilbert space $\mathscr{H}$. On a more practical note, unitary transformations are important in that they correspond to changes of representation: because a unitary transformation is bijective and conserves inner products, it is possible to interconvert reversibly from one representation to another without losing any information. In physics, this is especially helpful because it is often much more convenient to do a calculation in one representation than in another.

This is exactly what we are doing in converting to the so-called "interaction representation". The interaction representation is useful when we have a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_o + \hat{V}(t) \tag{4.154}$$

where the static Hamiltonian is (relatively) tractable to deal with, but the "perturbation" $\hat{V}(t)$ is difficult. Let the time-evolution operator corresponding to the total Hamiltonian $\hat{H}(t)$ be denoted $\hat{U}(t, t_o)$ and consider the unitary transformation $\mathscr{U}_o(t, t_o)$ defined by the unitary operator $\hat{U}_o^{-1} = e^{-\frac{\hat{H}_o}{i\hbar}(t - t_o)}$ which corresponds to the *inverse* of the time-evolution operator specified by $\hat{H}_o$ in the absence of $\hat{V}(t)$. Given an arbitrary vector $|\psi(t)\rangle = \hat{U}(t, t_o)\,|\psi(t_o)\rangle$ we

---

[20]Actually, a subtle difference has been glossed over: we have defined a unitary operator to be necessarily linear, while we have not made any such requirement on the transformation $\mathscr{U}$. In fact, the linearity of the transformation $\mathscr{U}$ follows from the three properties already listed, so that the correspondence is unambiguous. (See M. H. Stone, pg. 76).

assign an image vector $|\psi(t)\rangle_I = \hat{U}_o^{-1}(t, t_o)\,|\psi(t)\rangle = \hat{U}_o^{-1}(t, t_o)\hat{U}(t, t_o)\,|\psi(t_o)\rangle$. Mathematically this simply defines (at any time t) a unitary transformation on $\mathscr{H}$, while physically it corresponds to the "backwards" time-evolution which would occur in the absence of the perturbation $\hat{V}(t)$. Because the mapping is unitary, if we know the state of the system in the transformed (interaction) representation, we likewise know the state in the untransformed "Schrödinger") representation.

For this representation to be useful, we need to know how the vector $|\psi(t)\rangle_I$ evolves in time. Using the definition in terms of $|\psi(t)\rangle$ and taking the time-derivative of $|\psi(t)\rangle_I$ gives

$$
\begin{aligned}
\frac{d}{dt}\,|\psi(t)\rangle_I &= \frac{d}{dt}\left(\hat{U}_o^{-1}(t, t_o)\,|\psi(t)\rangle\right) \\
&= \frac{d}{dt}\left(\hat{U}_o^{-1}(t, t_o)\right)\hat{U}(t, t_o)\,|\psi(t_o)\rangle + \hat{U}_o^{-1}(t, t_o)\frac{d}{dt}\left(\hat{U}(t, t_o)\right)|\psi(t_o)\rangle
\end{aligned}
\tag{4.155}
$$

Recall that $\hat{U}_o(t, t_o)$ satisfies the TDSE under the static Hamiltonian $\hat{H}_o$, i.e. $\frac{d}{dt}\hat{U}_o(t, t_o) = \frac{1}{i\hbar}\hat{H}_o\hat{U}_o(t, t_o)$. To calculate the time-derivative of the adjoint operator $\hat{U}_o(t, t_o)$ note that[21]

$$
\begin{aligned}
\frac{d}{dt}\hat{U}_o^{-1}(t, t_o) &= \frac{d}{dt}\hat{U}_o^{\dagger}(t, t_o) = \left(\frac{d}{dt}U_o(t, t_o)\right)^{\dagger} \\
&= \left(\frac{1}{i\hbar}\hat{H}_o\hat{U}_o(t, t_o)\right)^{\dagger} = -\frac{1}{i\hbar}\hat{U}_o^{\dagger}(t, t_o)\hat{H}_o^{\dagger} \\
&= -\frac{1}{i\hbar}\hat{U}_o^{-1}(t, t_o)\hat{H}_o
\end{aligned}
$$

which gives

---

[21] In the derivation, we have made use of a few properties which have not been explicitly pointed out yet. First, note that for a linear operator $\hat{A}(t)$ we have

$$
\frac{d}{dt}\hat{A}^{\dagger}(t) = \left(\frac{d}{dt}\hat{A}(t)\right)^{\dagger}
\tag{4.156}
$$

since by definition of the adjoint for orthonormal basis vectors $|m\rangle$ and $|n\rangle$

$$
\begin{aligned}
\langle m|\,\frac{d}{dt}\hat{A}^{\dagger}(t)\,|n\rangle &= \frac{d}{dt}\,\langle m|\,\hat{A}^{\dagger}(t)\,|n\rangle = \frac{d}{dt}\,\langle n|\,\hat{A}(t)\,|m\rangle^* \\
&= \langle n|\,\frac{d}{dt}\hat{A}(t)\,|m\rangle^* = \langle m|\left(\frac{d}{dt}\hat{A}(t)\right)^{\dagger}|n\rangle,
\end{aligned}
\tag{4.157}
$$

where we have used the fact that

$$
\langle m|\,\hat{A}\,|n\rangle = \left\langle \hat{A}^{\dagger}m\,\middle|\,n\right\rangle = \langle n|\,\hat{A}^{\dagger}\,|m\rangle^*.
\tag{4.158}
$$

Second, recall that for two operators $\hat{A}$ and $\hat{B}$ the adjoint of the product operator is

$$\frac{d}{dt}\ket{\psi(t)}_I = -\frac{1}{i\hbar}\hat{U}_o^{-1}(t,t_o)\hat{H}_o\hat{U}(t,t_o)\ket{\psi(t_o)} + \frac{1}{i\hbar}\hat{U}_o^{-1}(t,t_o)\hat{H}(t)\hat{U}(t,t_o)\ket{\psi(t_o)}$$

$$= -\frac{1}{i\hbar}\hat{U}_o^{-1}(t,t_o)\hat{H}_o\hat{U}(t,t_o)\ket{\psi(t_o)} + \frac{1}{i\hbar}\hat{U}_o^{-1}(t,t_o)\left[\hat{H}_o + \hat{V}(t)\right]\hat{U}(t,t_o)\ket{\psi(t_o)}$$

$$= \frac{1}{i\hbar}\hat{U}_o^{-1}(t,t_o)\hat{V}(t)\hat{U}(t,t_o)\ket{\psi(t_o)}$$

$$= \frac{1}{i\hbar}\hat{U}_o^{-1}(t,t_o)\hat{V}(t)\hat{U}_o(t,t_o)\hat{U}_o^{-1}(t,t_o)\hat{U}(t,t_o)\ket{\psi(t_o)}$$

$$= \frac{1}{i\hbar}\left[\hat{U}_o^{-1}(t,t_o)\hat{V}(t)\hat{U}_o(t,t_o)\right]\ket{\psi(t_o)}_I \tag{4.162}$$

Notice now that the final equation has exactly the form of the Schrödinger equation with a new Hamiltonian $\hat{U}_o^{-1}(t,t_o)\hat{V}(t)\hat{U}_o(t,t_o)$ driving the time-evolution. In other words if we define an "interaction representation" potential $\hat{V}_I(t)$ as

$$\hat{V}_I(t,t_o) \equiv \hat{U}_o^{-1}\hat{V}(t)\hat{U}_o(t,t_o) \tag{4.163}$$

the time-evolution equation for $\ket{\psi(t)}_I$ becomes the so-called "Interaction Picture" Schrödinger equation

$$\frac{d}{dt}\ket{\psi(t)}_I = \frac{1}{i\hbar}\hat{V}_I(t)\ket{\psi(t)}_I. \tag{4.164}$$

In short, by introducing the unitary transformation $\hat{U}_o(t,t_o)^{-1}$ on the vectors of the system and replacing the perturbing potential $\hat{V}(t)$ with a "transformed" operator $\hat{V}_I(t)$, we have derived a "transformed" TDSE in the new representation which likewise defines the dynamics of our system. Remember that if we solve the time-evolution of this new TDSE to obtain $\ket{\psi(t)}_I$, we can at any time perform the inverse transformation $\hat{U}_o(t,t_o)$ to obtain the original Schrödinger representation vector $\ket{\psi(t)}$.

$$\left(\hat{A}\hat{B}\right)^\dagger = \hat{B}^\dagger\hat{A}^\dagger \tag{4.159}$$

because for arbitrary vectors $\ket{\psi}$ and $\ket{\phi}$ we have

$$\left\langle\psi\middle|\left(\hat{A}\hat{B}\right)\phi\right\rangle = \left\langle\hat{A}^\dagger\psi\middle|\hat{B}\phi\right\rangle = \left\langle\left(\hat{B}^\dagger\hat{A}^\dagger\right)\psi\middle|\phi\right\rangle.$$

Finally, for a complex number λ and a linear operator $\hat{A}$ note that

$$\left(\lambda\hat{A}\right)^\dagger = \lambda^*\hat{A}^\dagger \tag{4.160}$$

since for arbitrary vectors $\ket{\phi}$ and $\ket{\psi}$

$$\bra{\psi}\left(\lambda\hat{A}\right)^\dagger\ket{\phi} = \left\langle\lambda\hat{A}\psi\middle|\phi\right\rangle = \lambda^*\left\langle\hat{A}\psi\middle|\phi\right\rangle = \bra{\psi}\left(\lambda^*\hat{A}^\dagger\right)\ket{\phi}. \tag{4.161}$$

In deriving Eq. (4.164) we have made the conversion $\hat{V}(t) \rightarrow \hat{V}_I(t)$ as essentially an "ansatz" simply because we saw that we would obtain a Schrödinger-like equation if we did. In fact there is a deeper reason for making the definition $\hat{V}_I(t) = \hat{U}_o^{-1}(t, t_o)\hat{V}(t)\hat{U}_o(t, t_o)$. In our earlier discussion of unitary transformations, we specified a mapping of vectors onto other vectors, but did not comment on the effect of the transformation on operators. In principle, of course, we need not do anything to the operators: since a unitary transformation maps vectors within the same Hilbert space, we are free to operate on transformed vectors with un-transformed operators. For example, the operation

$$\hat{H}(t) \ket{\psi(t)}_I = \hat{H}(t)\hat{U}_o^{-1}(t, t_o) \ket{\psi(t)}$$

is perfectly well defined. However, it should be clear that the action of the un-transformed operators on the transformed vectors will be quite different than the action of un-transformed operators on the original un-transformed vectors, i.e. for an arbitrary (possibly time-depenent) linear operator $\hat{A}(t)$ and vector $\ket{\psi}$, the vector $\hat{A}(t) \ket{\psi(t, t_o)}_I$ need not bear any particular relation to the vector $\hat{A}(t) \ket{\psi(t, t_o)}$. This is why, for example, it is *not* valid to simply re-write the Schrödinger equation with the transformed interaction representation vectors and the un-transformed operators:

$$\frac{d}{dt} \ket{\psi(t)}_I \neq \frac{1}{i\hbar}\hat{H}(t) \ket{\psi(t)}_I$$

On the other hand, if we transform the set of *operators* as well according to the relation

$$\hat{A}_I(t) \equiv \hat{U}_o^{-1}(t, t_o)\hat{A}(t)\hat{U}_o(t, t_o), \tag{4.165}$$

we find that we can transform operator equations back and forth between the two representations completely reversibly. Consider a generic operator-vector equation

$$\hat{A} \ket{\psi} = \hat{B} \ket{\phi}$$

Applying a unitary transformation $\hat{T}$ to each side of the expression preserves the equality (each expression is a vector, so the transformation is well-defined), so we can write

$$\hat{T}\hat{A} \ket{\psi} = \hat{T}\hat{B} \ket{\phi} \, .$$

This equation is true, but it is not especially useful since what we really want is an equality in terms of the transformed vectors $\ket{\psi}_T = \hat{T} \ket{\psi}$ and $\ket{\phi}_T = \hat{T} \ket{\phi}$. To get the equation in this form, we insert between the operators and the vector they act on the identity operator $\hat{1} = \hat{T}^{-1}\hat{T}$:

$$\hat{T}\hat{A}\hat{T}^{-1}\hat{T} \ket{\psi} = \hat{T}\hat{B}\hat{T}^{-1}\hat{T} \ket{\phi}$$
$$\rightarrow \hat{A}_T \ket{\psi}_T = \hat{B}_T \ket{\phi}_T$$

In case we have multiple operators on one side, we simply insert the identity between each operator as well. For example, suppose that $\hat{A} = \hat{C}\hat{D}$; then the transformed operator expression is

$$\hat{A}_T = \hat{T}\left(\hat{C}\hat{D}\right)\hat{T}^{-1}$$
$$= \hat{T}\hat{C}\hat{T}\hat{T}^{-1}\hat{D}\hat{T}^{-1}$$
$$= \hat{C}_T\hat{D}_T.$$

The point here is that given an equality in one representation, we can transform it directly to another representation by transforming vectors according to the definition

$$|\psi\rangle_T = \hat{T}|\psi\rangle \qquad (4.166)$$

and the operators according to the definition

$$\hat{A}_T = \hat{T}\hat{A}\hat{T}^{-1}. \qquad (4.167)$$

As an example, notice that we can re-derive the interaction representation TDSE in exactly this manner. Starting with the Schrödinger equation

$$\frac{d}{dt}|\psi(t)\rangle = \frac{1}{i\hbar}\hat{H}(t)|\psi(t)\rangle,$$

we apply $\hat{U}_o(t,t_o)^{-1}$ and insert the identity operator $\hat{U}_o(t,t_o)\hat{U}_o(t,t_o)^{-1}$ between each pair of terms to obtain

$$\hat{U}_o(t,t_o)^{-1}\frac{d}{dt}\left(\hat{U}_o(t,t_o)\hat{U}_o(t,t_o)^{-1}|\psi(t)\rangle\right) = \frac{1}{i\hbar}\hat{U}_o(t,t_o)^{-1}\hat{H}(t)\hat{U}_o(t,t_o)\hat{U}_o(t,t_o)^{-1}|\psi(t)\rangle$$

$$\rightarrow \hat{U}_o(t,t_o)^{-1}\frac{d}{dt}\left(\hat{U}_o(t,t_o)|\psi(t)\rangle_I\right) = \frac{1}{i\hbar}\hat{H}_I(t)|\psi(t)\rangle_I.$$

Splitting up the derivative on the left-hand side using the product rule (again generalized for operator-vector "products" as earlier) and on the right distributing the definition $\hat{H} = \hat{H}_o + \hat{V}(t)$, we obtain

$$\hat{U}_o(t,t_o)^{-1}\hat{U}_o(t,t_o)\frac{d}{dt}|\psi(t)\rangle_I + \hat{U}_o(t,t_o)^{-1}\left(\frac{d}{dt}\hat{U}_o(t,t_o)\right)|\psi(t)\rangle_I = \frac{1}{i\hbar}\left(\left[\hat{H}_o(t)\right]_I + \hat{V}_I(t)\right)|\psi(t)\rangle_I$$

$$\rightarrow \frac{d}{dt}|\psi(t)\rangle_I - \frac{1}{i\hbar}\hat{U}_o(t,t_o)^{-1}\hat{H}_o(t)\hat{U}_o(t,t_o)|\psi(t)\rangle_I = \frac{1}{i\hbar}\left(\left[\hat{H}_o(t)\right]_I + \hat{V}_I(t)\right)|\psi(t)\rangle_I$$

$$\rightarrow \frac{d}{dt}|\psi(t)\rangle_I = \frac{1}{i\hbar}\hat{V}_I(t)|\psi(t)\rangle_I.$$

Note in particular that this ability to transform operator expressions from one representation to another means that we can calculate expectation values in any frame just by

replacing all operators and vectors with their transformed counter-parts. For example, we have

$$\langle\phi|\,\hat{A}\,|\psi\rangle = \langle\phi|\,\hat{U}_o(t,t_o)\hat{U}_o^{-1}(t,t_o)\hat{A}\hat{U}_o(t,t_o)\hat{U}_o^{-1}(t,t_o)\,|\psi\rangle = {}_I\langle\phi|\,\hat{A}_I\,|\psi\rangle_I. \qquad (4.168)$$

This further highlights the equivalence of dynamics in any transformation frame: as long as we know how to convert back and forth from one representation to another, which representation we use is entirely at our discretion.

Before moving on, it is worth pausing to note that nothing in the transformation to the interaction representation required that $\hat{H}_o$ be static in time. Everything developed above could be just as easily applied to an arbitrary Hamiltonian $\hat{H} = \hat{H}_1(t) + \hat{H}_2(t)$ where $\hat{H}_1(t)$ and $\hat{H}_2(t)$ are arbitrary Hermitian operators (in particular, they need not commute with each other or with themselves at different times). The reason for introducing the interaction representation under a static Hamiltonian is that this is where the approach is most useful since in this case we can obtain an analytical expression for $\hat{U}_o(t,t_o)$. Of course we have already shown that an anlytical expression (in terms of the eigenstates of $\hat{H}_o$) would also exist for $\hat{U}_o(t,t_o)$ in the case that $\hat{H}_o(t)$ is time-dependent but commutes with itself at all times. In this case also transformation to the interaction representation will prove useful (and follows exactly the same procedure as used above) as we will see later on in the context of the classical bath.

4.3.4 Perturbative Expansion

We've shown in the last section that introducing a unitary transformation to the interaction representation allows us to view the time-evolution of our system according to the transformed Schrödinger equation Eq. (4.164). The power of this approach is that the interaction representation vectors $|\psi(t)\rangle_I$ already contains the time-evolution due to the static Hamiltonian $\hat{H}_o$. For example, if the perturbtation $\hat{V}(t)$ were zero, Eq. (4.164) would tell us that $|\psi(t)\rangle_I$ would be stationary in time. So all time-evolution in the interaction representation is entirely due to the perturbation $\hat{V}(t)$. In cases where the "magnitude" of $\hat{V}(t)$ is small compared with the time-scale over which we observe the system,[22] we similarly expect that $|\psi(t)\rangle \approx |\psi(t)\rangle_I$ since the perturbing potential $\hat{V}(t)$ only modifies the dynamics slightly. It is in exactly this circumstance where the operator expansion demonstrated earlier for $\hat{U}(t,t_o)$ becomes useful. Define an interaction representation time-evolution operator $\widetilde{U}_I(t,t_o)$ via[23]

$$|\psi(t)\rangle_I = \widetilde{U}_I(t,t_o)\,|\psi(t_o)\rangle_I = \widetilde{U}_I(t,t_o)\,|\psi(t_o)\rangle, \qquad (4.169)$$

i.e. $\widetilde{U}_I(t,t_o)$ is the solution to the interaction picture Schrödinger equation Eq. (4.164) recast as an operator differential equation (note that we have made use of the fact that

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[23]In particular, we want the magnitude of the integral of $\hat{V}(t)$ (which has units of $energy \cdot time$) to be small compared to Planck's constant $\hbar$ which appears in the denominator of each expansion term.

[23]The reason for not denoting this as $\hat{U}_I(t,t_o)$ is that it is *not* the transformed operator $\hat{U}_o^{-1}(t,t_o)\hat{U}(t,t_o)\hat{U}_o(t,t_o)$ which would be suggested by this notation.

$|\psi(t_o)\rangle_I = |\psi(t_o)\rangle$ since $\hat{U}_o(t_o, t_o) = \hat{1}$). Note that the full dynamics of the system (in the Schrödinger representation) are then given by

$$\hat{U}(t, t_o) = \hat{U}_o(t, t_o)\widetilde{U}_I(t, t_o) \tag{4.170}$$

since

$$|\psi(t)\rangle = \hat{U}(t, t_o)|\psi(t_o)\rangle = \hat{U}_o(t, t_o)|\psi(t)\rangle_I = \hat{U}_o(t, t_o)\widetilde{U}_I(t, t_o)|\psi(t_o)\rangle_I$$
$$= \hat{U}_o(t, t_o)\widetilde{U}_I(t, t_o)|\psi(t_o)\rangle . \tag{4.171}$$

We can now directly apply the Dyson expansion Eq. (4.152) to the interaction representation TDSE (Eq. (4.164))to obtain

$$\widetilde{U}_I(t, t_o) = \sum_n \left(\frac{1}{i\hbar}\right)^n \int_{t_o}^t dt_1 \int_{t_o}^{t_1} dt_2 ... \int_{t_o}^{t_{n-1}} dt_n \hat{V}_I(t_1)\hat{V}_I(t_2)...\hat{V}_I(t_n). \tag{4.172}$$

What is different about our use of the expansion here compared to earlier is that in this case we are working under the assumption that $\hat{V}_I(t)$ is in some sense a "weak" perturbation. As a result, we can often truncate the expansion after only a few terms. For example, we might introduce a first order approximation to the true dynamics via

$$\widetilde{U}_I^{(1)}(t, t_o) = \hat{1} + \frac{1}{i\hbar}\int_{t_o}^t dt_1 \hat{V}_I(t_1) \tag{4.173}$$

The total dynamics of the system in the Schrödinger picture are then approximated (to an accuracy depending on the "strength" of $\hat{V}(t)$) by

$$\hat{U}(t, t_o) \approx \hat{U}_o(t, t_o)\widetilde{U}_I^{(1)}(t, t_o)$$
$$= \hat{U}_o(t, t_o) + \frac{1}{i\hbar}\hat{U}_o(t, t_o)\int_{t_o}^t dt_1 \hat{V}_I(t_1).$$

It is exactly this type of approximation which we will introduce to study spectroscopy. Usually we will consider a system with a stationary Hamiltonian $\hat{H}_o$ which will then be perturbed by the electromagnetic field $\hat{V}(t)$ of our laser pulse, white light, microwave beam, etc. Linear response of the system refers to the evolution of the system due to the term on the far right of the equation above (which is linear in the perturbation). Higher-order terms in the Dyson expansion give rise to non-linear response, which become important as the magnitude of the perturbation (i.e. intensity of the electro-magnetic field) increases. Before moving on to detailed spectroscopic considerations, we return to the density matrix formalism to show how the perturbative expansion can be applied to the time-propagation of $\hat{\rho}(t)$.

4.3.5   Density Matrices Revisited

With the matrial just developed, we are ready to return to the density matrix representation introduced at the start of our discussion. One advantage of casting quantum dynamics in terms of time-evolution operators is that we can simply write down an expression for the time-dependent density matrix by inspection. Since we know that $|\psi(t)\rangle = \hat{U}(t, t_o)$ and $\hat{\rho}(t) = \sum_i p_i |\chi(t)\rangle \langle \chi(t)|$ we obtain immediately

$$\hat{\rho}(t) = \sum_i p_i \hat{U}(t, t_o) |\chi(t_o)\rangle \langle \chi(t_o)| \hat{U}^\dagger(t, t_o)$$

$$= \hat{U}(t, t_o) \hat{\rho}(t_o) \hat{U}^\dagger(t, t_o). \tag{4.174}$$

For example, if the system is evolving under a static Hamiltonian $\hat{H}_o$, we have $\hat{U}(t, t_o) = exp\{\frac{\hat{H}_o(t-t_o)}{i\hbar}\}$ and

$$\hat{\rho}(t) = exp\left\{\frac{\hat{H}_o(t - t_o)}{i\hbar}\right\} \hat{\rho}(t_o) exp\left\{-\frac{\hat{H}_o(t - t_o)}{i\hbar}\right\}. \tag{4.175}$$

Taking matrix elements in the eigenbasis of $\hat{H}_o$ returns

$$\hat{\rho}_{mn}(t) = e^{\frac{E_m}{i\hbar}(t-t_o)} \hat{\rho}_{mn}(t_o) e^{-\frac{E_n}{i\hbar}(t-t_o)} = e^{\frac{E_m - E_n}{i\hbar}(t-t_o)} \hat{\rho}_{mn}(t_o) \tag{4.176}$$

just as obtained earlier from the quantum Liouville equation. Moreover, we can perform a transformation of the system dynamics to the Schrödinger representation exactly as above, applying the usual operator definition $\hat{\rho}_I(t) = \hat{U}_o^{-1}(t, t_o)\rho(t)\hat{U}_o(t, t_o)$ to obtain a transformed Liouville equation

$$\hat{U}_o^{-1}(t, t_o)\frac{d}{dt}\left(\hat{U}_o(t, t_o)\hat{U}_o^{-1}(t, t_o)\hat{\rho}(t)\hat{U}_o(t, t_o)\right) = \frac{1}{i\hbar}\hat{U}_o^{-1}(t, t_o)\left[\hat{H}, \hat{\rho}\right]\hat{U}_o(t, t_o)$$

$$\rightarrow \hat{U}_o^{-1}(t, t_o)\frac{d}{dt}\left(\hat{U}_o(t, t_o)\hat{\rho}_I(t)\right) = \frac{1}{i\hbar}\left[\hat{H}_I(t), \hat{\rho}_I(t)\right]$$

$$\rightarrow \hat{U}_o^{-1}(t, t_o)\left(\frac{1}{i\hbar}\hat{H}_o(t)\hat{U}_o(t, t_o)\hat{\rho}_I(t) + \hat{U}_o(t, t_o)\frac{d}{dt}\hat{\rho}_I(t)\right) = \frac{1}{i\hbar}\left[\hat{H}_I(t), \hat{\rho}_I(t)\right]$$

$$\rightarrow \frac{d}{dt}\hat{\rho}_I(t) = \frac{1}{i\hbar}\left[\hat{V}_I(t), \hat{\rho}_I(t)\right]$$

and similarly a perturbative expansion

$$\hat{\rho}_I(t) = \sum_{n=0}^{\infty} \frac{1}{(i\hbar)^n} \int_{t_o}^{t} dt_1 \int_{t_o}^{t_1} dt_2 ... \int_{t_o}^{t_{n-1}} dt_n \left[\hat{V}_I(t_1), \left[\hat{V}_I(t_2), ..., \left[\hat{V}_I(t_n), \hat{\rho}(t_o)\right]\right]\right]. \tag{4.177}$$

It is this perturbative expansion which we will largely make use of in our discussion of spectroscopy. Truncation of the sum at n^{th} order will be referred to as n^{th} order effects;

for low field (e.g. light) intensities, linear response is often sufficient to consider, while for higher order fields (e.g. produced by high-intensity or pulsed lasers) higher order terms will be important.