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AS.030.301 & AS.030.302  
PHYSICAL CHEMISTRY

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# FOREWORD

My goal here was to recreate everything a student needs to know for the physical chemistry sequence, *from the perspective of a student currently learning it*. Oftentimes there are topics Dr. Fried and/or Dr. Bowen take for granted cause they've been studying this stuff for years that went completely over my head during lecture and so understanding those things took a bit of extra thought. All of that extra thought I've transcribed here, in an effort to provide equally, if not more detailed explanations for the plethora of topics covered by thermodynamics, kinetics, and quantum mechanics.

I take no credit for any of the writing here. All of it was taken from the lectures of either class, the accompanying textbooks for the courses, or other interesting books I've read. Although I didn't cite any sources *within* the text, I provided references at the end. In addition to the fact that I'm not taking credit for anything, I think I'm good as far as plagiarism goes. Also I just learned that technically the University owns all of the classes/lecture material(?) so I guess I'm just gonna hope that the University doesn't sue me.

- Sam

## Part I

# Thermodynamics and Kinetics



## CHAPTER

# 1

# THE LAWS OF THERMODYNAMICS

*A theory is more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of basic concepts, it will never be overthrown.*

- Albert Einstein

The laws of thermodynamics put restrictions on how thermodynamic variables change when a system and its surroundings change. These restrictions include, but are not limited to, the flow of energy and the distribution of temperature in a material. In chemical reactions, the first and second laws determine the equilibrium positions of reactions.

Thermodynamics can be treated purely from a macroscopic point of view, treating its laws as being stated in terms of macroscopic variables and measurable properties. This approach is usually referred to as *classical thermodynamics*. Another approach is to derive the macroscopic behavior from a statistical treatment of the atoms and molecules composing the system, called *statistical thermodynamics*.

## 1.1 The First Law

One popular description of the first law is simply, *energy is conserved*. That is, energy can neither be created nor destroyed. For an isolated system, this result clearly holds. For more complicated processes, the internal energy of a system may increase or decrease but held in the context of the overall change in energy of the system and surroundings, the overall change in energy is zero. In other words, the change in energy of a system is exactly equal to the opposite change in energy of the surroundings.

The first law is sometimes represented with a statement that energy of the system can be changed either by heat or by work, and different combinations of heat and work can bring about a change of state<sup>1</sup>.

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<sup>1</sup>In fact, it was Joule who discovered heat and work were both forms of energy. Prior to the early 1800's, heat and work were thought to be completely distinct ideas

The statement of the first law in equation can be expressed elegantly, as

$$U = q + w \quad (1.1.1)$$

with  $U$  representing the internal energy of the system,  $w$  the work done *on* the system, and  $q$  the heat *absorbed* by the system. That is,  $w < 0$  when the system does work. It's also commonly expressed in its differential form.

$$dU = dq + dw \quad (1.1.2)$$

with  $dU$  as an exact differential whereas  $dq$  and  $dw$  are inexact differentials and dependent on the path. This fact that heat and work are *inexact* differentials is immensely important. A system at equilibrium possesses a uniquely determined amount of internal energy, but it makes no sense to talk about a system possessing a unique amount of heat or a certain amount of work.

## 1.2 The Second Law

The second law of thermodynamics establishes the concept of entropy as a state function and applies its physical properties to the direction of spontaneous change for a thermodynamic process. In particular, the second law helps us determine the spontaneity of processes, in contrast to the first law which says nothing about the direction of thermodynamically favorable change for a reaction. The importance of the second law cannot be understated. In fact, Arthur Eddington, an English physicist and mathematician, wrote the following in 1927:

If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation—well these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Analytically, the second law of thermodynamics can be expressed simply as

$$dS \geq 0 \quad (1.2.1)$$

where  $S$  is the entropy of the universe. More generally, the second law tells us that the entropy change for an isolated system must be positive <sup>2</sup>. Naturally, reversible processes neither increase nor decrease entropy. If one direction *decreased* entropy, then that direction would violate the second law.

As we'll come to see, the second law of thermodynamics puts a limit on the efficiency of engines that accept heat energy and output work. As a rough example, consider a power plant which accepts energy in the form of heat to be powered. In reality, only about 30% of the heat energy accepted by one of these plants is used as work and therefore 70% of it must be rejected at a lower temperature. In practice, this heat is typically absorbed by water and oftentimes taken from a natural source such as a river or lake. In this case, the resulting increase in temperature of the water reservoir has significant effects on aquatic life and has come to be known as "thermal pollution."

### 1.2.1 The Numerous Restatements and Corollaries of the Second Law

We know that entropy is a state function and therefore the entropy change for a reversible process is the same as the irreversible process with identical initial and final states. Thus,

$$\Delta S = \int \frac{dq_{rev}}{T} > \int \frac{dq_{irr}}{T} \quad (1.2.2)$$

---

<sup>2</sup>We can think of the entire universe as an isolated system, which is why we can make the broad statement that the entropy of the universe is always increasing

since  $q_{rev}$  is strictly greater than  $q_{irr}$ . Then, we have that

$$\Delta S \geq \int \frac{dq}{T} \quad (1.2.3)$$

where the equality holds for a reversible transformation but is a strict inequality for an irreversible transformation. This is known as the *Clausius Inequality*.

The Clausius inequality is one example of a restatement of the second law. Here are a few more:

In sticking with the theme of the legend himself Rudolf Clausius, we turn to the Clausius and Kelvin statements of the second law. These statements give the direction of spontaneous change for a transformation, either through heat flow or through the work done by heat engines. Although seemingly unrelated at first, these two statements imply one another. That is, if we can prove one the proof of the other is trivial. The Clausius statement of the second law is

No process is possible where the sole result is transfer of heat from a body at lower temperature to a body at higher temperature.

The Kelvin statement of the second law is

No process is possible where the sole result is absorption of heat from a reservoir and its complete conversion to work.

An important corollary to these statements is the following:

Systems can spontaneously undergo processes that decrease entropy, but this must be counteracted by an increase in entropy of the surroundings.

That is, it is certainly possible for systems to spontaneously become more ordered, but only when the surroundings become less ordered to an equal or greater extent. An alternative (and potentially more useful way of phrasing this result) is that

Any spontaneous (irreversible) process that occurs in isolation must be associated with increasing entropy.

In order to understand the Kelvin statement of the second law of thermodynamics (and therefore also the Clausius statement) and develop a connection to entropy, we'll need to understand heat engines and the Carnot cycle, which are covered in Section 3.4.1.

Another (arguably even more convoluted) restatement of the second law is *Planck's statement of the second law*, put forth as follows:

It is impossible to devise a machine whose only effects are the removal of heat from a reservoir and the performance of work.

Okay this the last restatement of the second law I promise: Caratheodory<sup>3</sup> formulated the second law of thermodynamics not based on physical quantities such as heat but instead through the axiomatic principle of irreversibility in thermodynamics:

In the neighbourhood of any initial state, there are states which cannot be approached arbitrarily close through changes of state.

In this statement he went on to coin the term *adiabatic accessibility*, the principle that two states  $X$  and  $Y$  are said to be “adiabatically accessible” if  $X$  can be transformed to  $Y$  without the system suffering from the transfer of energy as heat or matter<sup>4</sup>

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<sup>3</sup>Constantin Caratheodory was a Greek mathematician who contributed to everything from complex analysis to thermodynamics. To quote some old German book about him, “He was remembered by his colleagues as a respectable and cultured man.”

<sup>4</sup>Obviously the principle is more technical than this but it's way beyond anything that we would ever need to know for this class.

### 1.2.2 Schrödinger's "Paradox"

According to the second law, all isolated systems are expected to reach a system of maximum disorder after a long enough time has passed. Since life approaches and maintains a highly ordered state some argue that this seems to violate the aforementioned law, implying a paradox. Schrödinger, however, pointed out that the biosphere is *not* an isolated system and that there is an increase in entropy in the surroundings as a result of the loss of heat to an organism's environment. By this mechanism, the second law is obeyed and life maintains a highly ordered state which is sustained by an increase in disorder of the universe.

In order to increase order on earth, as life does, organisms harness the free energy provided by the sun.

## 1.3 The Third Law

The third law of thermodynamics concerns itself with the convergence of the entropy of a system. In particular, the behavior of substances at *absolute zero*, or zero Kelvin. In words, the third law can be written as

The entropy of a system is zero at absolute zero.

Pretty simple. Microscopically, this result agrees with our intuition about entropy. Consider the Boltzmann equation,  $S = k_B \ln W$  where  $W$  is the number of microstates for a system. For a system at absolute zero, by definition there is no kinetic energy among atoms or molecules and therefore no movement. Then, the number of microstates reduces to one and entropy reduces to zero.

Interestingly, there exists a formulation of the third law which approaches the subject by postulating the behavior of energy:

If the composition of two thermodynamic systems constitutes an isolated system, then any energy exchange between the two systems is bounded.

Sometimes the third law is referred to as *Nernst's Theorem* because he was the first person to postulate a result like this. If we wanted to be as general as possible about the third law, assuming nothing about the behavior of atoms and molecules at absolute zero, then we could write alternatively that at absolute zero the entropy of a system is a well-defined constant and is determined by the degeneracy of the ground state of the system.

After the development of statistical mechanics, the third law of thermodynamics went from being a *fundamental law* to a *derived law*, as the result that substances at absolute zero have zero entropy is a consequence of the Boltzmann equation.

## CHAPTER

# 2

# STATE FUNCTIONS AND THEIR STATE VARIABLES

*In science we must all submit not to what seems to us attractive from one point of view or another, but to what represents an agreement between theory and experiment.*

- Dmitri Mendeleev

*State functions* are path independent functions, meaning that their values can be defined for a specific set of conditions. Examples of some common thermodynamic state functions include the internal energy  $U$  and the enthalpy  $H$ . An important property of state functions is that they enjoy the equality of mixed partial derivatives. This property will be of great use when we derive the Maxwell relations.

The *state variables* of a state function are those which are necessary to completely describe the value of a state function. Typically, the variables which we'll be interested in are temperature, pressure, and volume.

For reactions containing more than one chemical species, we are often interested in the *molar quantity*, denoted  $\tilde{X}$ , and *partial quantity*, denoted  $X_i$  of a particular species. The molar quantity is the amount of a particular extensive thermodynamic quantity contributed *per mole*, and the partial quantity is the amount of a particular thermodynamic quantity contributed by *one substance*. Using these definitions, we can define a *partial molar quantity* as  $\tilde{X}_i$  which represents the amount of a particular thermodynamic quantity contributed per mole by one substance in a mixture.

## 2.1 Internal Energy

The internal energy of a system is conserved, forming the basis of the first law of thermodynamics. It is characterized by the heat absorbed and the work done on a system. Mathematically, it can be expressed as

$$U \equiv q + w \quad (2.1.1)$$

We could also get more technical with our expression for the internal energy and write it in a differential form,

$$dU = dq + dw \quad (2.1.2)$$

or an integrated form

$$\Delta U = \int dq + \int dw \quad (2.1.3)$$

Although the internal energy is the sum of two path dependent quantities (heat and work), by itself it is a state function meaning that  $\Delta U$  along a closed curve (i.e., the initial and final states are the same) is equal to zero.

The natural variables of internal energy are  $V$  and  $S$ . This implies that at a constant volume and entropy, the internal energy of a system is an indicator of spontaneity.

This relationship can be shown using the differential form of the First Law:

$$\begin{aligned} dU &= dq + dw \\ &\leq TdS - PdV \\ &= \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \end{aligned} \quad (2.1.4)$$

Note that we'll use an equality and assume that this transformation is reversible. Here, we'll take a moment to gaze at Equation (2.1.4). Considering the inequality,  $dU$  acts as a useful potential when  $dS$  and  $dV$  are zero, that is, when  $S$  and  $V$  are fixed. When this happens, the direction of spontaneous change is the one which *decreases* internal energy (this direction is the one consistent with the Second Law of Thermodynamics). Moreover, when  $dU = 0$  the system has reached equilibrium.

Here would be a good time to point out the contrast between determining spontaneity in thermodynamic systems and simple mechanical systems. Why is it that when we talk about spontaneity in thermodynamic systems we use Gibbs free energy but when we talk about spontaneity for mechanical systems we can get away with talking about just the energy?

For simple mechanical systems, we are typically interested in situations involving only a few objects: A ball rolling down a hill, an object rotating about an axis, or a projectile being launched off a cliff, to name a few. In these cases, the entropy of the system barely changes (if at all) and can therefore be treated as constant. In a similar vein, the volume of these systems doesn't change whatsoever. Then, as we've already posited, when entropy and volume are constant then the internal energy of a system will be an indicator of spontaneity.

In contrast, for thermodynamic systems the entropy of a transformation is nearly impossible to hold constant (still possible, just *nearly* impossible). For a chemical reaction, the expansion of a gas, the mixing of two substances, the entropy is always changing. Moreover, the volume changes in many of these transformations as well. Thus, we see that the internal energy of a substance is a very poor indicator of spontaneity for thermodynamic systems because of its *natural variables*.

State functions acting as potentials under certain conditions will be a common theme as we analyze different types of free energy. Alright, now we can return to our analysis of the internal energy:

In the last line after Equation (??) is the total partial differential of  $U$  and is there to (hopefully) clearly illustrate the relationships

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \& \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Then, by the equality of mixed partial derivatives, we have

$$\begin{aligned} \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V &= \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S \\ \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \end{aligned} \quad (2.1.5)$$

Which is one of the four Maxwell relations.

## 2.2 Enthalpy

The enthalpy is defined as

$$H \equiv U + PV \quad (2.2.1)$$

and was created just because we needed a state function with a differential equal  $dU + PdV$  at a constant pressure. The enthalpy can be thought of as the internal energy plus the cost of pushing back the universe to make a hole in which to place (or expand) the system. Enthalpy is useful for analyzing the thermodynamics of systems *at constant pressure*. At a constant pressure, the total partial differential of  $H$  becomes

$$\begin{aligned} dH &= \left( \frac{\partial H}{\partial U} \right)_{P,V} dU + \left( \frac{\partial H}{\partial P} \right)_{V,U} dP + \left( \frac{\partial H}{\partial V} \right)_{P,U} dV \\ &= dU + PdV \end{aligned}$$

and by the First Law of Thermodynamics we can say that  $(dH)_P = (dq)_P$ . Why did we go to all this trouble? Recall that we define the heat capacity at a constant pressure as  $dq/T = C_p$ . Thus,

$$C_p = \left( \frac{\partial H}{\partial T} \right)_P \quad (2.2.2)$$

I think I do this derivation somewhere else in these notes too.

We'll quickly jump back to the total partial differential of the enthalpy, this time deriving it from how we define  $H$ :

$$\begin{aligned} H &= U + PV \\ dH &= dU + d(PV) \\ &= dq + dw + PdV + VdP \\ &\leq TdS - PdV + PdV + VdP \\ &\leq TdS + VdP \\ &= \left( \frac{\partial H}{\partial S} \right)_P dS + \left( \frac{\partial H}{\partial P} \right)_S dP \end{aligned} \quad (2.2.3)$$

Equation (2.2.3) indicates that under conditions with *constant entropy and pressure*, enthalpy acts as an indicator of spontaneity. In particular, if  $dH < 0$  in these conditions, the transformation is spontaneous. Similar to when we talked about internal energy, this is the direction which obeys the Second Law of Thermodynamics. Moreover, if  $dH = 0$  under these conditions we know that we've achieved equilibrium.

For now, however, we'll substitute an equality and assume the transformation is reversible. Thus, we see that the natural variables of enthalpy are  $P$  and  $S$  so that  $H(P, S)$ . Notice that

$$\left( \frac{\partial H}{\partial S} \right)_P = T \quad \& \quad \left( \frac{\partial H}{\partial P} \right)_S = V$$

so that by the equality of mixed partial derivatives,

$$\begin{aligned} \frac{\partial}{\partial P} \left( \frac{\partial H}{\partial S} \right)_P &= \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial P} \right)_S \\ \left( \frac{\partial T}{\partial P} \right)_S &= \left( \frac{\partial V}{\partial S} \right)_P \end{aligned} \quad (2.2.4)$$

which is one of the four Maxwell relations.

## 2.3 Entropy

Entropy is a physical property of a system that corresponds to randomness, disorder, or uncertainty. Typically, entropy is defined in the context of the second law of thermodynamics at the macroscopic level, but it can also be viewed from the microscopic level using the Boltzmann equation. Macroscopically, we define the entropy as

$$dS \equiv \frac{dq_{rev}}{T} \quad (2.3.1)$$

where  $dq_{rev}$  is the heat absorbed by a system during a reversible transformation. Since entropy is a state function, however, we can define it for both reversible and irreversible processes:

$$\Delta S_{rev} = \Delta S_{irr} = \int \frac{dq_{rev}}{T} \quad (2.3.2)$$

Then, if asked to compute the entropy involved in an irreversible process, we can go about computing the entropy for the reversible process which has identical initial and final states.

Here, recall the important result that the heat absorbed by a system for a reversible process is always less than that for an irreversible process. That is,  $q_{rev} > q_{irr}$ . This implies that

$$\Delta S_{rev} = \Delta S_{irr} = \frac{dq_{rev}}{T} > \frac{dq_{irr}}{T} \quad (2.3.3)$$

and we obtain the *Clausius inequality*, a restatement of the second law of thermodynamics:

$$\Delta S \geq \int \frac{dq}{T} \quad (2.3.4)$$

This expression is an equality for a reversible process and a strict inequality for a irreversible process.

The Clausius inequality has some major implications. For an adiabatic process (or an isolated system),  $dq = 0$  and therefore  $\Delta S \geq 0$ . This inequality forms the basis of the second law of thermodynamics. Since the universe as a whole can be considered an isolated system we can make the broad claim that *the entropy of the universe never decreases*.

A potentially more helpful way of phrasing this result is that *any spontaneous (irreversible) process that occurs in isolation must be associated with an increase in entropy*. Naturally, reversible processes neither increase nor decrease entropy. If one direction were to increase entropy the corresponding reverse reaction would be associated with a decrease in entropy and would therefore violate the second law.

Another important corollary to these statements is that *systems can spontaneously undergo processes which decrease the entropy of the system as long as the transformation increases the entropy of the surroundings to an equal or greater extent*.

As we noted above, since entropy is a state function the total change in entropy for the system remains the same for a reversible and irreversible transformation as long as the transformations have the same initial and final states. Naturally we can ask the question, how does the entropy change for the *surroundings* differ for a reversible transformation versus an irreversible one, if at all?

Recall that the heat absorbed by a system in a reversible reaction is strictly greater than the heat absorbed in the corresponding irreversible reaction. That is,  $q_{rev} > q_{irr}$ . Therefore, for an irreversible reaction, some of the energy of the system must be *lost* to the surroundings as heat. Then,  $dq_{sur,irr} > 0$  and therefore  $dS_{sur} > 0$ . Thus, *the entropy change for the surroundings is greater during an irreversible reaction than it is for the corresponding reversible reaction*.

### 2.3.1 Entropy Change for Four Fundamental Changes of State

As we've mentioned previously, although the entropy is defined for reversible processes, we can use that definition for any sort of change of state because entropy is a state function. In fact, we can find the change in entropy



for our four favorite transformations of state. Here they are without justification:

Entropy Changes for Fundamental Transformations	
Reversible <i>Isochoric</i> Change of State	$\Delta S = C_V \ln \left( \frac{T_f}{T_i} \right)$
Reversible <i>Isobaric</i> Change of State	$\Delta S = C_P \ln \left( \frac{T_f}{T_i} \right)$
Reversible <i>Isothermal</i> Change of State	$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right)$
Reversible <i>Adiabatic</i> Change of State	$\Delta S = 0$

Now here are their justifications:

1. *Reversible Isochoric Process.* Here, volume is fixed and reversibility is achieved by raising the temperature of the surroundings slowly, allowing heat to flow into the system to maintain thermal equilibrium.

For an isochoric process,  $w = 0$  and so all of the internal energy of a system is in the form of heat. Thus,

$$dq_{rev} = dU = C_V dT$$

and so we can evaluate the change in entropy as

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_i}^{T_f} \frac{C_V dT}{T} = C_V \ln \left( \frac{T_f}{T_i} \right) \quad (2.3.5)$$

(note that we can factor  $C_V$  out of the integral for ideal gasses because it will never vary with temperature).

Notice, unlike heat flow which increases linearly as  $T_f$  increases in constant pressure expansion, entropy increases logarithmically.

2. *Reversible Isobaric Process.* Recall that reversible isobaric expansion involves substantial heat flow into the system in order to keep the pressure of the system matched with the constant pressure of the surroundings.

To evaluate the entropy change of reversible isobaric heating we'll quickly derive a relationship between heat flow and temperature change. Recall that we define the enthalpy as  $H = U + PV$ . Then,

$$\begin{aligned} dH &= dU + d(PV) = dq_{rev} + dw_{rev} + PdV + VdP \\ &= dq_{rev} - PdV + PdV + 0 \\ &= dq_{rev} \end{aligned}$$

In step 2 we made the substitution  $dw = -PdV$  and also  $VdP = 0$  because the transformation is isobaric. Additionally, recall that  $dH = C_P dT$ . So, the change in entropy can be computed as

$$\Delta S = \int \frac{dq_{rev}}{T} = \int_{T_i}^{T_f} \frac{C_P dT}{T} = C_P \ln \left( \frac{T_f}{T_i} \right) \quad (2.3.6)$$

For an ideal gas, we can rewrite this as

$$\Delta S = C_P \ln \left( \frac{V_f}{V_i} \right) \quad (2.3.7)$$

which shows how the largest entropy changes occur during expansions when the system is highly compressed. Similar to isochoric heating, whereas heat flow increases linearly with a constant pressure, entropy increases logarithmically. However, the proportionality constants differ, as  $C_P > C_V$ . Thus, a given temperature increase at a constant pressure results in a larger entropy increase than at a constant volume.

3. *Reversible Isothermal Process.* For ideal gasses,  $\Delta U = 0$  which implies that  $dq_{rev} = -dw_{rev}$ . Fortunately,

we have an expression for  $dw_{rev}$ , allowing us to compute the change in entropy with relative ease:

$$\begin{aligned}
 \Delta S &= \int \frac{dq_{rev}}{T} = \int \frac{-dw_{rev}}{T} = \int \frac{PdV}{T} \\
 &= \int \frac{nRTdV}{VT} \\
 &= nR \int_{V_i}^{V_f} \frac{dV}{V} \\
 &= nR \ln \left( \frac{V_f}{V_i} \right)
 \end{aligned} \tag{2.3.8}$$

4. *Reversible Adiabatic Heating.* As long as adiabatic expansion is reversible, Equation (2.3.2) requires that there is no change in entropy since  $dq_{rev} = 0$  along the entire adiabat. Because entropy remains constant, reversible adiabatic transformations can be regarded as *isentropic*.

What about the entropy change for irreversible transformations? Let's consider the irreversible expansion of a gas against a vacuum. Above we identified that entropy change for the reversible isothermal expansion of a gas to be

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right)$$

What is different in the irreversible case where the external pressure is zero (the vacuum)? Firstly, there can be no work done on the surroundings because there is no external pressure. Secondly, there is no heat absorbed or emitted by the system because the surroundings are a vacuum. Hence,  $\Delta U = 0$  (which is consistent with the isothermal reaction of an ideal gas) and the system must remain along an isotherm during this transformation, implying that  $PV$  is constant. Thus, for this irreversible expansion, we have that

$$\Delta S = nR \ln \left( \frac{V_f}{V_i} \right) = nR \ln \left( \frac{P_i}{P_f} \right)$$

Another important thing to note about this scenario which contrasts its reversible counterpart is the entropy change of the surroundings. For the reversible expansion,  $\Delta S_{univ} = 0$  (as for any reversible process) because although the system absorbs heat as it expands ( $\Delta S > 0$ ), it simultaneously does work on its surroundings ( $\Delta S < 0$ ) and we're in accordance with the second law of thermodynamics.

For the irreversible transformation, however, the expansion against a vacuum can be thought of as an isolated system (a vacuum is nothing, after all). Thus, there are no surroundings to counteract the positive change in entropy of the system and therefore

$$\Delta S_{sys} = \Delta S_{univ} > 0$$

which is consistent with the process being spontaneous.

### 2.3.2 The Microscopic View of Entropy

So far we've dealt with entropy from a macroscopic level, considering heat flow through a system. A far more profound definition for entropy comes from statistical mechanics in the form of the Boltzmann equation. Mathematically, it can be expressed as

$$S = k_B \ln \Omega \tag{2.3.9}$$

where  $k_B = R/N_A \approx 1.381 \times 10^{-23}$  J/K is the Boltzmann constant and  $\Omega$  is the number of microstates for a system. Interestingly, this equation is engraved on Ludwig Boltzmann's tombstone in Vienna, Austria.

Let's consider the simplified example of the expansion of a gas in a lattice: For a lattice with  $L$  spaces

available to occupy and  $N$  total molecules within the lattice, there are

$$\binom{L}{N} = \frac{L!}{N!(L-N)!}$$

total ways to arrange the (indistinguishable) molecules. Considering the expansion of a gas, we can think of the initial volume containing  $L_1$  lattice cells and the final volume containing  $L_2$  lattice cells. The change in entropy can be computed using the Boltzmann equation:

$$\begin{aligned}\Delta S = S_f - S_i &= k_B \ln \binom{L_2}{N} - k_B \ln \binom{L_1}{N} \\ &= k_B \left[ \ln \left( \frac{L_2! N! (L_1 - N)!}{N! L_1! (L_2 - N)!} \right) \right] \\ &= k_B \ln \left( \frac{L_2! (L_1 - N)!}{L_1! (L_2 - N)!} \right)\end{aligned}$$

This expression is not very computationally friendly. We can simplify this result using *Stirling's Approximation*,

$$\ln(x)! = x \ln x - x$$

which becomes more accurate as  $x$  becomes larger. There is a more technical version of this approximation but I'm not really concerned with that. Approximations are lame to begin with.

Let's apply this formula to our expression above (I'm gonna omit some of the algebra because I trust myself to be able to do it any other time):

$$\begin{aligned}\frac{\Delta S}{k_B} &= \ln \left( \frac{L_2! (L_1 - N)!}{L_1! (L_2 - N)!} \right) \\ &= \ln(L_2)! + \ln(L_1 - N)! - \ln(L_1)! - \ln(L_2 - N)! \\ &\approx L_2 \ln(L_2) + (L_1 - N) \ln(L_1 - N) - L_1 \ln(L_1) - (L_2 - N) \ln(L_2 - N) \\ &= L_2 \ln \left( \frac{L_2}{L_2 - N} \right) + L_1 \ln \left( \frac{L_1 - N}{L_1} \right) - N \ln \left( \frac{L_1 - N}{L_2 - N} \right)\end{aligned}$$

In the majority of physical systems, a container of gas will be mostly empty so that  $L_1, L_2 \gg N$  and we can simplify our approximation as

$$\begin{aligned}\frac{\Delta S}{k_B} &\approx L_2 \ln \left( \frac{L_2}{L_2} \right) + L_1 \ln \left( \frac{L_1}{L_1} \right) - N \ln \left( \frac{L_1}{L_2} \right) \\ \Rightarrow \Delta S &= k_B N \ln \left( \frac{L_2}{L_1} \right)\end{aligned}$$

If we say that each lattice cell has volume  $V_L$  then  $V_2 = L_2 V_L$  and  $V_1 = L_1 V_L$  so that

$$\Delta S = k_B N \ln \left( \frac{V_2}{V_1} \right) = nR \ln \left( \frac{V_2}{V_1} \right) \quad (2.3.10)$$

which agrees exactly with our formulation for the entropy change at the macroscopic level. To make the final substitution above note that  $N_A k_B = R$  and that  $N_A = N/n$  where  $N$  is the number of molecules and  $n$  is the number of moles.

## 2.4 Free Energy

Free energy can be defined as the maximum amount of work a thermodynamic process can do at a constant temperature and its sign indicates whether or not the process is spontaneous (this is true for both the Helmholtz and Gibbs free energy; both have temperature as a natural variable and are tied to the work done during a

reaction).

The basic definition of free energy is a measure of a system's ability to cause change. Free energy, in slight contrast, is the measure of a system's ability to do work at a constant temperature, i.e., the "useful" energy.

### 2.4.1 Helmholtz Free Energy

The Helmholtz free energy <sup>1</sup>, defined before the Gibbs free energy, is defined as

$$A \equiv U - TS \quad (2.4.1)$$

and is an indicator of spontaneity for processes which occur at a constant volume and temperature, as indicated by the total partial differential of  $A$ :

$$dA = \left( \frac{\partial A}{\partial V} \right)_T dV + \left( \frac{\partial A}{\partial T} \right)_V dT \quad (2.4.2)$$

The Helmholtz free energy is useful for gas-phase reactions or for isolated systems kept at a constant volume. This is the main distinction between the Helmholtz and Gibbs free energies: While Helmholtz energy is useful for reactions at a constant volume, say, a transformation within a bomb calorimeter, the Gibbs energy is useful for transformations at a constant pressure where  $\Delta H = q$ .

### 2.4.2 Gibbs Free Energy

Gibbs free energy is defined as

$$G \equiv H - TS \quad (2.4.3)$$

and is an indicator of spontaneity for processes which occur at a constant pressure and temperature, as indicated by the total partial differential of  $G$ :

$$dG = \left( \frac{\partial G}{\partial P} \right)_T dP + \left( \frac{\partial G}{\partial T} \right)_P dT \quad (2.4.4)$$

The Gibbs free energy is an invaluable measure for thermodynamic processes, as most take place at a constant  $P$  and  $T$ . In fact,  $G$  is independent of the  $PdV$  work needed to "make space for additional molecules" and therefore equals the work *not* associated with system expansion or compression *at a constant temperature*. Hence, it has immense utility for solution-phase chemistry.

The quantities for each partial derivative of  $G$  can be found as follows:

$$\begin{aligned} dG &= dH - d(TS) = d(U + PV) - d(TS) \\ &= dU + d(PV) - d(TS) \\ &= dq + dw + PdV + VdP - TdS - SdT \\ &= TdS - PdV + PdV + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned}$$

Thus, we find

$$\left( \frac{\partial G}{\partial P} \right)_T = V \quad \& \quad \left( \frac{\partial G}{\partial T} \right)_P = -S$$

---

<sup>1</sup>The designation  $A$  for the Helmholtz free energy comes from the German word for work, *arbeit*. This makes sense with the context that free energy is the maximum amount of work a process can do at a constant temperature.

## 2.5 Spontaneity

Any system that does not evolve over time is said to be at equilibrium. Otherwise, the direction of evolution is the *spontaneous direction*. A *spontaneous process will occur without additional work being done on the system*. Most spontaneous processes are irreversible, and the processes that are spontaneous and reversible must be spontaneous in both directions, in accordance with the second law of thermodynamics.

Spontaneity does not imply that the process occurs immediately. Rather, that it will occur with a very high probability once the barrier of change is overcome. Take the combustion of wood into carbon dioxide and water as an example. The process can only begin at very high temperatures but once it does it will proceed until all of the wood is used.

One of the driving forces behind a spontaneous process is the spreading out of energy as heat rather than through work. In developing a new state function that allows us to predict the direction of this energy dispersion, we can utilize the first law of thermodynamics. Because heat flow is a key factor in the spontaneous direction, we can write the first law as follows, for an ideal gas undergoing reversible changes to volume and temperature:

$$\begin{aligned} dq_{rev} &= dU - dw_{rev} \\ &= C_V(T)dT + PdV \\ &= C_V(T)dT + \frac{nRT}{V}dV \end{aligned} \quad (2.5.1)$$

Recall that in order for a function to be a state function its mixed partial derivatives must be equal. So, let's test that:

$$\left( \frac{\partial C_V(T)}{\partial V} \right)_T \neq \left( \frac{\partial (nRT/V)}{\partial T} \right)_T$$

So close! Notice, however, that if we divide both sides of the equation by  $T$  we can make it so these partials are equal:

$$\left( \frac{\partial C_V(T)/T}{\partial V} \right)_T = \left( \frac{\partial (nRT/VT)}{\partial T} \right)_T = 0$$

Thus,  $dq_{rev}/T$  is a state function that we define as *entropy*:

$$dS = \frac{dq_{rev}}{T} \quad (2.5.2)$$

In contrast to the macroscopic view of spontaneity mentioned above we can also discuss and analyze the *microscopic* view of spontaneity and see how the two approaches are connected.

As an example, consider a mixture of 1 mole of a unique molecule and 1 mole of a different molecule in a lattice where the members of each species are indistinguishable. If we distributed the molecules such that one species occupied one half of the box and the other species occupied the other half of the box then there would only be one microstate for the system. In contrast, if we allowed each species to occupy anywhere on the lattice (affording more of a “mixed” state), there are many more possible arrangements of molecules in space.

The microstates consistent with a description of “mixed” are not necessarily more likely to occur, however, there are vastly more arrangements that can be described as mixed than those that cannot. From a probability standpoint, then, the likelihood of being in the “mixed” state is much greater because of the number of arrangements that are mixed.

Thus, given enough time to explore all such microstates which are mixed or nonmixed, at equilibrium a system will be mixed because it is much more likely to occupy that state.

### 2.5.1 Criteria for Spontaneity

There are numerous criteria for spontaneity depending on the conditions of the system and which properties of a substance are being held constant, if any. Below is a table illustrating the different conditions and system

could be under and the corresponding indicator of spontaneity:

Criteria for Spontaneity	
Indicator	Condition
$dS \geq 0$	Isolated system ( $dq = dw = 0$ )
$dU \leq 0$	Constant entropy $S$ and volume $V$
$dH \leq 0$	Constant entropy $S$ and pressure $P$
$dF \leq 0$	Constant volume $V$ and temperature $T$
$dG \leq 0$	Constant pressure $P$ and temperature $T$

As we can see from above, entropy is an indicator of spontaneity when the system is isolated, that is, when neither matter nor energy is exchanged between the system and its surroundings. This agrees with our intuition behind the second law of thermodynamics because the universe itself can be considered an isolated system. In reality, however, the reactions we deal with are not often isolated. So, we need a better indicator of spontaneity for most thermodynamic processes: Enter Gibbs free energy.

Okay I lied about Gibbs free energy entering I'm gonna make a quick aside first. Notice that under a constant *temperature* we should immediately focus on the free energy of a system. Meanwhile, under a constant entropy (which will pretty much only ever happen when considering mechanical systems) we'll shift our focus away from free energy and instead focus on the internal energy and enthalpy. These are easy rules to keep in mind, not as easy as when to use the entropy as an indicator of spontaneity though, which can be considered in nearly every case as having some effect on the spontaneity of a reaction. Now, enter Gibbs free energy.

As we can see from the table above, the Gibbs free energy is an indicator of spontaneity at a constant pressure and temperature, 2 variables which can be held constant for a thermodynamic system with relative ease. In fact, this is the case because the pressure and temperature are oftentimes interacting with the pressure and temperature of the surroundings which are more or less constant over the course of a reaction. Although we could use any of the other state functions to indicate spontaneity for *any* sort of process, there is oftentimes a clear choice as to which will be the best.

With this idea in mind, consider what might make a good indicator for a simple mechanical system, composed of a few moving parts. If you've taken an introductory physics class you'll know that we use the internal energy of a system  $U$  to indicate spontaneity in this case. Why? For a simple mechanical system, the entropy virtually does not change since the number of microstates are limited with so few "particles" ("particles" in this case being the macroscopic objects). Moreover, the volume of the system will likely not change (consider the example of rolling a ball down a hill; there's no volume change whatsoever here). Thus, the internal energy of the system will be a great indicator of spontaneity.

The relationships described above will be illustrated whilst deriving the Maxwell relations in the following section.

## 2.5.2 Some Spontaneity Questions

I've begun studying for finals. Here are some questions regarding spontaneity. For each scenario, state whether it is certainly, not necessarily, or certainly not spontaneous and provide a brief justification.

1. *Under constant temperature and pressure, an ideal polymer expands to its maximal extension.* At a constant temperature and pressure we'll want to consider the Gibbs free energy associated with this process. Recall that we define the change in Gibbs free energy as

$$\Delta G = \Delta H - T\Delta S$$

In the case of extension, we can assume that  $\Delta H \ll \Delta S$  because although there might be some change in enthalpy due to changing intermolecular reactions, it is nowhere near the change in entropy. Moreover, we know that the entropy change will be large and positive since extension is associated with fewer arrangements

and microstates. Then, by Boltzmann's equation, the entropy change will be negative. Hence,  $\Delta G$  will be (potentially very) large and positive and this reaction will *certainly not be spontaneous*.

2. *Under a constant temperature, an ideal gas expands to its maximal volume.* This reaction is *certainly spontaneous*. First, just by using the example of what we observe in everyday life, we know that gasses expand to fill their containers (spontaneously). So, if I were to go into a Macy's and get sprayed by those people who spray the perfume, the perfume wouldn't just idly in the place I was standing, it would diffuse throughout the store! Figure 2.1 is provided for any visual learners.



Figure 2.1: Me running through a Macy's.

Now, a more thermodynamic approach. Notice that with the *expansion* of a gas, there will be a greater number of microstates associated with the final (larger) volume than with the initial (smaller) volume. Hence, by Boltzmann's equation we have that the change in entropy must be positive and therefore this reaction is always spontaneous.

Now, another more thermodynamic approach. Notice that this system is isolated so that we can use the entropy of the isothermal expansion to predict spontaneity. Then,

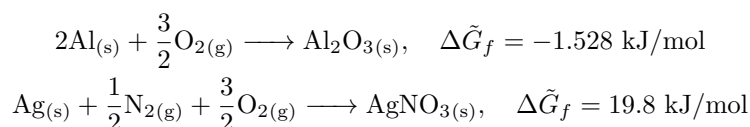
$$\begin{aligned} dS &= \frac{dq}{T} = \frac{-dw}{T} = \frac{P_{ext}dV}{T} = \frac{nR}{V}dV \\ \Delta S &= nR \int_{V_i}^{V_f} \frac{dV}{V} \\ &= nR \ln \left( \frac{V_f}{V_i} \right) \end{aligned}$$

Hence, the change in entropy is positive since  $V_f > V_i$  and the reaction is certainly spontaneous.

3. *Under a constant temperature and pressure, a chemical reaction proceeds in which the products are more "ordered" than the reactants.* Constant temperature and pressure should immediately sound the alarm for using Gibbs free energy. Similar to the first question, recall that

$$\Delta G = \Delta H - T\Delta S$$

so that the Gibbs energy is dependent on two quantities, enthalpy and entropy. Now, for just a moment consider the following two reactions:



Clearly, both of these reactions have a decrease in entropy, based off of the number of products and their

phases. However, the signs of the Gibbs free energies of formation are different! That is all to say, there can be a decrease in entropy for a chemical reaction which is spontaneous. Hence, this is *not necessarily spontaneous*.

4. *Under constant temperature and pressure, a chemical system where the species are at their equilibrium concentrations returns to the standard state conditions.* I mean I feel like this one is obvious. Clearly, work must be done on the system in order for it to progress *away* from equilibrium. In fact, if movement in one direction away from equilibrium were spontaneous and therefore movement in the other direction were not spontaneous, we'd be violating the second order of thermodynamics. Thus, this is *certainly not spontaneous*.
5. *At  $T = 273.15\text{ K}$ , water transforms entirely from liquid to solid.*

## 2.6 Maxwell Relations

The Maxwell relations are a system of partial differential equations which relate thermodynamic quantities which would typically be very difficult to measure. They can be derived from the equality of mixed partial derivatives and come from the definitions of the familiar thermodynamic potentials,  $U$ ,  $H$ ,  $F$ , and  $G$ .

It is important to note that these relations hold *for all reversible and irreversible processes*.

The four most common Maxwell relations utilize the definitions of the state functions named above. Here they are:

$$\frac{\partial^2 U}{\partial S \partial V} = \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (2.6.1)$$

$$\frac{\partial^2 H}{\partial S \partial P} = \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad (2.6.2)$$

$$\frac{\partial^2 F}{\partial T \partial V} = \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad (2.6.3)$$

$$\frac{\partial^2 G}{\partial T \partial P} = \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P \quad (2.6.4)$$



## CHAPTER

# 3

## HEAT AND WORK

*If there were matter so rare in the universe that we could only perform one measurement on it, we should measure its heat capacity.*

- Albert Einstein

### 3.1 Work

There are tons of ways work can be performed:

Work!

Type of Work	Intensive Variable	Extensive Variable	Differential Work, $dw$
Hydrostatic	Pressure, $P$	Volume, $V$	$-P_{ext}dV$
Surface	Surface Tension, $\gamma$	Area, $A$	$\gamma dA$
Elongation	Force, $F$	Length, $L$	$FdL$
Electrical	Potential Difference, $\varphi$	Electrical Charge, $Q$	$\varphi dQ$
Gravitational	Gravitational Potential, $gh$	Mass, $m$	$mgdh$

Most of the time we're interested in pressure-volume ( $PV$ ) work. Looking at this one in the table, why is there a negative for the differential work,  $dw = -P_{ext}dV$ ? Well, consider the cases in which volume could change: If  $\Delta V < 0$  then work is done *on* the gas and  $w > 0$ . Conversely, if  $\Delta V > 0$  the gas does work on the surroundings and so  $w < 0$ .

Aside from most of the time, the numerous other types of work show up often. Consider a mechanical example, involving the stretching of a spring. By Hookes' Law we have  $F = kx$  where  $k$  is some proportionality constant and  $x$  is the displacement from equilibrium for the spring (this scenario is represented as "Elongation" in the table above). Then, the work done is given by  $w = Fx$ , or  $dw = Fdx$  for some differential change in distance.

Another, I think more interesting example/problem, can come from considering the surface tension of a lipid vesicle and how it affects the surface area of the vesicle: Consider a lipid molecule which self-assembles

into a sphere whose shape is determined predominantly by the surface area and surface tension of the vesicle. Then, we're interested in the differential work  $dw = \gamma dA$ .

For a process carried out at a constant temperature and constant area, let's write down a condition for spontaneity in terms of free energy. To do this we'll consider the Helmholtz free energy:

$$\begin{aligned} F &= U - TS \\ dF &= dU - d(TS) \\ &= dq + dw - TdS - SdT \\ &\leq TdS + \gamma dA - TdS - SdT \\ dF &\leq \gamma dA - SdT \end{aligned}$$

Thus, at a constant area and temperature, we see that the condition for spontaneity is simply  $dF \leq 0$ .

Now, suppose that the internal energy and entropy of the vesicle are given by the following expressions:

$$\begin{aligned} U(A, \gamma) &= \frac{\gamma}{A_0} (A - A_0)^2 \\ S(A) &= k_B \ln(A/a) \end{aligned}$$

for some initial area  $A_0$  and a real number  $a$ . Write down an expression for  $F$ , the Helmholtz free energy of the system: To do this, all we have to consider is the functional form of the Helmholtz free energy we already wrote above. Thus,

$$\begin{aligned} F &= U - TS \\ F(A, \gamma) &= \frac{\gamma}{A_0} (A - A_0)^2 - T[k_B \ln(A/a)] \end{aligned}$$

which is the final answer. Notice that we've expressed the Helmholtz free energy as a function of *only*  $A$  and  $\gamma$ .

Now, suppose that I'm interested in how to measure

$$\left( \frac{\partial \gamma}{\partial T} \right)_A$$

but that I'm incapable of varying the temperature for some reason. Is there an alternate expression we could use to compute this partial derivative? Yes.

Recognize that we can use the Maxwell relation for the Helmholtz free energy,

$$\left( \frac{\partial^2 F}{\partial A \partial T} \right) = \left( \frac{\partial^2 F}{\partial T \partial A} \right)$$

by recognizing that  $(\partial F / \partial A)_T = \gamma$  and  $(\partial F / \partial T)_A = -S$ . Thus, we have that

$$\left( \frac{\partial \gamma}{\partial T} \right)_A = - \left( \frac{\partial S}{\partial A} \right)_T$$

We can take the derivative of  $S$  with respect to  $A$  at a constant temperature in the expression above to afford the simple expression

$$\left( \frac{\partial \gamma}{\partial T} \right)_A = - \frac{k_B}{A}$$

### 3.1.1 Irreversible Expansion of an Ideal Gas

## 3.2 Heat

### 3.2.1 Heat Capacities

Heat capacity is defined as the amount of heat necessary to cause a unit change in the temperature of the substance. Symbolically, this can be written as

$$C \equiv \frac{dq}{dT} \quad (3.2.1)$$

Since  $C$  is a function of heat (an inexact differential), the heat capacity of a substance depends on the path of a transformation.

Note that for an ideal gas, we can take the heat capacity of a substance to be constant. In contrast, the heat capacity of a real gas will be a function of temperature.

The heat capacity of a system heated at a constant volume,  $C_V$  differs from that at a constant pressure,  $C_P$ . Both are state functions, but they represent two *different* state functions. Thus, it is important to specify between the two:

$$C_V = \left( \frac{dq}{dT} \right)_V \quad \& \quad C_P = \left( \frac{dq}{dT} \right)_P$$

Note that  $C_P > C_V$  for any substance. Why? To rephrase the question, we're interested in why it takes more heat to raise the temperature of a gas under a constant pressure than it does under a constant volume. The difference is that at a constant volume, the gas can't do work so that all of the heat goes into kinetic energy, i.e., raising the temperature. In contrast, at a constant pressure, the gas can do work on the surroundings and so some heat will also cause the gas to expand.

The importance and relevance of heat capacity cannot be stressed enough. The flow of heat appears explicitly in the first law of thermodynamics and therefore the heat capacity, a quantity which directly relates the flow of heat to the temperature at which a process is occurring, warrants particular attention.

Since  $dq$  is an inexact differential we'd like an alternative definition for  $C_V$  and  $C_P$  based on something that is more easily calculable, such as a state function. Let's begin by trying to rewrite  $C_V$  in terms of a state function: Notice that at a constant volume we can rewrite the first law as

$$(dU)_V = dq + dw = dq$$

since there can be no work done due to the fact that the volume is unchanging ( $dV = 0$ ). Thus, we can express the internal energy as

$$(dU)_V = dq = C dT$$

$$\left( \frac{\partial U}{\partial T} \right)_V = C_V(T) \quad (3.2.2)$$

which gives us a relationship between the internal energy and the heat capacity at a constant volume. Notice that this result is *general*. That is, for *any* transformation of an ideal gas we can use this relationship since  $U$  is path independent. This idea wrinkled my brain for a while, but I recommend looking at some example problems regarding transformations of an ideal gas, drawing the transformations on a  $PV$  diagram, and finding a path where we can definitively say that this equality holds no matter what. In fact, here's an example:

*PV shenanigans*

Let's return to heat capacities. In particular, let's try to find an analogous expression for  $C_P$  as we did with  $C_V$  above. Whenever we think about constant pressures, enthalpy should be the first thing that pops into

our minds. So, let's run with that. Consider a differential change in enthalpy:

$$\begin{aligned}
 dH &= dU + d(PV) \\
 &= dq + dw + d(PV) \\
 &= dq - PdV + PdV + VdP \\
 &= dq + VdP
 \end{aligned}$$

at a constant pressure, we have that

$$\begin{aligned}
 (dH)_P &= dq = C dT \\
 \left( \frac{\partial H}{\partial T} \right)_P &= C_P(T)
 \end{aligned} \tag{3.2.3}$$

which affords the relationship between heat capacity at a constant pressure and enthalpy that we were looking for. Similar to the Equation (3.2.2), this result is *general*. In a manner similar to how we “proved” it above, try to convince yourself that we can use this result for the transformation of *any* ideal gas.

### 3.2.2 The Heat Capacity Ratio

For an ideal gas, the heat capacity of a substance is constant with temperature. In fact, we can relate the heat capacity at a constant pressure to that at a constant volume with the *Mayer's relation*:

$$C_P - C_V = nR \tag{3.2.4}$$

using molar heat capacities this takes the form  $\tilde{C}_P - \tilde{C}_V = R$ . As a result, if we know the heat capacity at a constant pressure for an ideal gas we can immediately determine its heat capacity at a constant volume.

Another relationship we are often interested in is the ratio of these heat capacities, namely

$$\gamma = \frac{\tilde{C}_P}{\tilde{C}_V} = \frac{C_P}{C_V} \tag{3.2.5}$$

(I believe I hint at this relation in Section ?? on adiabatic transformations. Refer to that section for this relations utility I guess). Two values of  $\gamma$  that come up often are those for a monatomic and diatomic ideal gas and are worth remembering:

$$\begin{aligned}
 \text{For a monatomic gas,} \quad \gamma &= 5/3 \\
 \text{For a diatomic gas,} \quad \gamma &= 7/5
 \end{aligned}$$

Both of these relations stem from the following facts about ideal gasses:

	Monatomic Gas	Diatomic Gas
$C_P$	$3nR/2$	$5nR/2$
$C_V$	$5nR/2$	$7nR/2$

I already mentioned this but its worth repeating: *The heat capacity at a constant pressure is always greater than the heat capacity at a constant volume for all substances.* That is,  $C_P > C_V$  always. This guarantees that  $\gamma > 1$  for all substances.

Interestingly, we can alternatively compute  $\gamma$  for an ideal gas using the degrees of freedom  $f$  of a monatomic or diatomic gas:

$$\gamma = 1 + \frac{2}{f} \tag{3.2.6}$$

For a monatomic gas, an atom has 3 degrees of freedom: It can translate in any of the  $x$ ,  $y$ , or  $z$  directions. Thus,  $\gamma = 5/3$  for a monatomic gas as written above. For a diatomic gas, the molecule has all of the translational

freedom as does a monatomic gas, however, it has the added ability to stretch in the direction of either atom, affording 5 degrees of freedom. Then,  $\gamma = 7/5$  for a diatomic gas as posited above.

Now, what about real gasses? For real gasses, the main difference is that the heat capacity is a function of temperature, as noted above. However, as the temperature increases (or decreases) both  $C_P$  and  $C_V$  increase (or decrease) at a similar rate so that Mayer's relationship *becomes a good guess*, that is,  $C_P - C_V \approx nR$ . This constant difference reflects the relatively constant  $PV$  work done during a transformation at a constant pressure versus at a constant volume.

Unlike their difference, the ratio between  $C_P$  and  $C_V$  *decreases* with an increasing temperature. Since both heat capacities increase as the temperature increases,

$$\gamma = \frac{C_P}{C_V} \rightarrow 1 \text{ as } T \rightarrow \infty$$

Using Equation (3.2.6), this result should make some intuitive sense because as the temperature increases the number of degrees of freedom a substance has increases as well.

Importantly, keep in mind that this limit *does not hold* for ideal gasses because the heat capacities of an ideal gas are unchanging. Then, the ratio of  $C_P/C_V$  will remain the same always for an ideal gas.

### 3.3 Fundamental Changes of State

Without any explanation, here are expressions for work and heat for the four most common fundamental changes of state we'll encounter *for an ideal gas*:

Work and Heat for Different Changes of State

Condition	Work Done on System	Heat Absorbed by System	$\Delta U$
Isobaric	$-P\Delta V$	$\int_{T_i}^{T_f} C_P dT = C_P \Delta T$	$\int_{T_i}^{T_f} C_P dT - P\Delta V$
Isochoric	0	$\int_{T_i}^{T_f} C_V dT = C_V \Delta T$	$\int_{T_i}^{T_f} C_V dT$
Isothermal	$-nRT \ln(V_f/V_i)$	$nRT \ln(V_f/V_i) = -w$	0
Adiabatic	$C_V \Delta T$	0	$C_V \Delta T$

#### 3.3.1 Reversible Isobaric Transformations

A reversible isobaric transformation is a constant pressure process that can occur spontaneously in either direction without additional work being done on the system.

We'll first consider the work done during one of these processes: Reversible constant pressure-volume change results in a very simple work calculation when the external pressure is constant:

$$w = - \int P_{ext} dV = -P_{ext} \int dV = -P_{ext} \Delta V$$

For a quasistatic process we can assume  $P_{sys} = P_{ext}$  and simplify this result as

$$w = -P\Delta V \quad (3.3.1)$$

Expansion involves  $\Delta V > 0$  which agrees with our intuition that the expansion of an ideal gas does work on the surroundings.

Comparing reversible isobaric expansion to reversible isothermal expansion, it should make intuitive sense that  $\Delta T > 0$  in the former, since isobars move through higher temperature isotherms during expansion. To understand this temperature increase we'll consider the expansion of a gas on a molecular level. Because the number of moles of gas is constant, at a larger volume the gas density is lower and therefore to maintain a constant pressure the gas molecules must be imbued with more energy to maintain the same frequency of collisions. In order to give these molecules more energy there must be a temperature increase.

Now we'll consider the heat flow during one of these processes: When an ideal gas expands at a constant pressure, the appropriate heat capacity is  $C_P$ . Moreover, it cuts upward through isotherms on the  $PV$  diagram and is therefore associated with an increase in temperature. We'll start by rearranging Equation (3.2.1) and using  $C_P$ :

$$dq = C_P dT$$

$$q = \int_{T_i}^{T_f} C_P dT$$

The solution to this integral will depend on how the heat capacity changes with temperature. For most systems,  $C_P$  can vary greatly even across large temperature ranges. However, over small temperature ranges (those often encountered in a laboratory) the heat capacity can be treated as independent of the temperature so that we can evaluate the integral with ease:

$$q = C_P \int_{T_i}^{T_f} dT = C_P(T_f - T_i) \quad (3.3.2)$$

Additionally, it's important to note that for ideal gasses,  $C_P$  (and  $C_V$ , for that matter) is constant<sup>1</sup>. We can also rewrite the change in internal energy of the system using this expression for heat and our expression for work during a reversible isobaric transformation, Equation (3.3.1):

$$\Delta U = q + w = C_P \Delta T - P \Delta V \quad (3.3.3)$$

### 3.3.2 Reversible Isochoric Transformations

A reversible isochoric transformation is a constant volume process that can occur spontaneously in either direction without additional work being done on the system.

First we'll consider the work done during one of these processes: When the pressure of a gas is increased at a constant volume, no work is done. If we try to evaluate the work integral,

$$w = - \int P_{ext} dV = 0 \quad (3.3.4)$$

because  $dV = 0$  for an isochoric process.

Now we'll consider the heat flow during one of these processes: The heat flow for a constant volume process can be analyzed in the same way as the constant pressure transformation, using  $C_V$  instead of  $C_P$ :

$$q = \int_{T_i}^{T_f} C_V dT = C_V \Delta T \quad (3.3.5)$$

Similar to above, the second equality holds only when  $C_V$  is not a function of temperature. In a constant volume process (and also dealing with an ideal gas), since there is no work done on the surroundings the change in internal energy of the system can be written as

$$\Delta U = \int dq = C_V \Delta T$$

Once again, we see that the internal energy of an ideal gas is a function of only the temperature. This fact holds in general and is worth remembering.

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<sup>1</sup>For monatomic gasses,  $C_P = 5nR/2$  and  $C_V = 3nR/2$ . For diatomic gasses,  $C_P = 7nR/2$  and  $C_V = 5nR/2$ . In both cases  $C_P - C_V = nR$ . This is a fact that will come in handy whenever we deal with ideal gasses.

### 3.3.3 Reversible Isothermal Transformations

A reversible isothermal transformation is a constant temperature process that can occur spontaneously in either direction without additional work being done on the system.

First we'll consider the work done during one of these processes: When a gas expands isothermally, there is an associated change in pressure and therefore pressure is not constant like it was in the isobaric case. To get around this, we can use the ideal gas law to evaluate the work integral:

$$w = - \int P_{ext} dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln(V) \Big|_{V_i}^{V_f} = -nRT \ln \left( \frac{V_f}{V_i} \right)$$

Thus,

$$w = -nRT \ln \left( \frac{V_f}{V_i} \right) \quad (3.3.6)$$

for the isothermal expansion of an ideal gas.

Expansion of a system causes  $V_f > V_i$  so that the logarithm in the final step is positive which is associated with negative work done on the system and positive work done on the surroundings which agrees with our intuition about work associated with the expansion of a gas.

For isotherms, heat must flow into the system during reversible expansion in order to keep the temperature constant. This is somewhat clear when comparing the curves in the  $PV$  diagram for isothermal expansion and adiabatic expansion. From a molecular perspective, the work done on the surroundings causes a loss in energy for the gas molecules, thereby decreasing the energy and temperature of the gas. Thus, to maintain temperature, heat must flow into the system.

Comparing reversible isobaric expansion to reversible isothermal expansion, it should make intuitive sense that  $\Delta T > 0$  in the former, since isobars move through higher temperature isotherms during expansion. To understand this temperature increase we'll consider the expansion of a gas on a molecular level. Because the number of moles of gas is constant, at a larger volume the gas density is lower and therefore to maintain a constant pressure the gas molecules must be imbued with more energy to maintain the same frequency of collisions. In order to give these molecules more energy there must be a temperature increase.

We could also make this argument using the First Law,  $dU = dq + dw$ . Since the internal energy of an ideal gas is dependent only on temperature, during an isothermal expansion we'd expect  $dU = 0$ . Since  $dw < 0$  we require that  $dq > 0$  in order to not break any fundamental laws of physics.

Now we'll consider the heat flow during one of these processes: For an isothermal expansion, there is no temperature change (as the name implies) and therefore  $dT = 0$ . So, we cannot employ the same method as above. Instead, recognize that for an ideal gas,  $\Delta U = 0$  (since  $U(T)$  is a function of temperature for an ideal gas) and so we have the equality

$$q = -w = nRT \ln \left( \frac{V_f}{V_i} \right) \quad (3.3.7)$$

which comes from the calculation done in Equation (3.3.6) for the work done during reversible isothermal expansion.

### 3.3.4 Reversible Adiabatic Transformations

A reversible adiabatic transformation is a process in which no heat is exchanged with the system's surroundings (that is,  $dq = 0$ ) that can occur spontaneously in either direction without additional work being done on the system.

First we'll consider the work done during one of these processes: Unlike any of the other state changes, an adiabatic transformation is more difficult to analyze because there is an associated change in pressure, volume, and temperature. For an adiabatic expansion, the heat flow is zero ( $dq = 0$ ) and so the change in internal energy is due to only the work performed during the transformation. So, in order to evaluate the work we need

an expression  $P = P(V)$ , that is, a functional expression for the pressure of the system in terms of only the volume.

The decrease in pressure for an adiabatic expansion of an ideal gas is similar to that of an isothermal expansion, however, the decrease is much sharper because the heat flow that is required to maintain constant temperature is prevented by the adiabatic boundary. This dependance suggests a decay of the form

$$P = \frac{\lambda}{V^\gamma}$$

for some proportionality constants  $\lambda$  and  $\gamma > 1$ .

From here, recognize that for a particular adiabat, the constant  $\lambda$  must remain unchanged at all points  $(P, V)$  on the  $PV$  diagram. Thus,

$$PV^\gamma = P_i V_i^\gamma$$

which affords an expression for the pressure as a function of the volume,

$$P = \frac{P_i V_i^\gamma}{V^\gamma} \quad (3.3.8)$$

Now we can plug this into the work integral:

$$\begin{aligned} w &= - \int P dV = - \int_{V_i}^{V_f} \frac{P_i V_i^\gamma}{V^\gamma} dV \\ &= -P_i V_i^\gamma \int_{V_i}^{V_f} \frac{dV}{V^\gamma} \\ &= -P_i V_i^\gamma \left[ -\frac{1}{(\gamma-1)V^{\gamma-1}} \right]_{V_i}^{V_f} \\ &= \frac{P_i V_i^\gamma}{\gamma-1} \left( \frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}} \right) \end{aligned}$$

This form can be used directly to compute the work done in an adiabatic process, but it's not super friendly. However, for an ideal gas we can take advantage of the fact that  $C_P - C_V = nR$  to simplify the expression above: Recall that  $\gamma = C_P/C_V$  so that

$$\begin{aligned} \frac{C_P - C_V}{C_V} &= \frac{nR}{C_V} \\ \gamma - 1 &= \frac{nR}{C_V} \end{aligned}$$

and we can substitute this result into our expression for the work:

$$\begin{aligned} w &= \frac{P_i V_i^{\frac{nR}{C_V} + 1}}{\frac{nR}{C_V}} \left( \frac{1}{V_f^{\frac{nR}{C_V}}} - \frac{1}{V_i^{\frac{nR}{C_V}}} \right) \\ &= \frac{P_i V_i C_V}{nR} \left[ \left( \frac{V_i}{V_f} \right)^{\frac{nR}{C_V}} - 1 \right] \end{aligned}$$



From here we'll utilize the ideal gas law and replace pressure with temperature and volume, giving

$$\begin{aligned} w &= \frac{nRT_i C_V}{nR} \left[ \left( \frac{V_i}{V_f} \right)^{\frac{nR}{C_V}} - 1 \right] \\ &= T_i C_V \left[ \left( \frac{V_i}{V_f} \right)^{\frac{nR}{C_V}} - 1 \right] \\ &= C_V \left[ T_i \left( \frac{V_i}{V_f} \right)^{\frac{nR}{C_V}} - T_i \right] \end{aligned}$$

Now for a little algebraic gymnastics. We've already shown why  $PV^\gamma = P_i V_i^\gamma$  for an adiabatic process, so briefly consider the adiabatic expansion of an ideal gas from  $(P_i, V_i)$  to  $(P_f, V_f)$ : Using the ideal gas law, we can express this relationship as

$$\begin{aligned} P_i V_i^\gamma &= P_f V_f^\gamma \\ \frac{nRT_i}{V_i} V_i^\gamma &= \frac{nRT_f}{V_f} V_f^\gamma \\ T_i V_i^{\gamma-1} &= T_f V_f^{\gamma-1} \\ T_f &= \left( \frac{V_i}{V_f} \right)^{\gamma-1} T_i \end{aligned}$$

Now we'll mess around with the exponent,  $\gamma - 1$  a little bit:

$$\gamma - 1 = \frac{C_P}{C_V} - 1 = \frac{C_P - C_V}{C_V} + \frac{C_V}{C_V} - 1 = \frac{nR}{C_V}$$

Why go about all this trouble? Well, we've just shown that

$$T_f = \left( \frac{V_i}{V_f} \right)^{\frac{nR}{C_V}} T_i$$

and so our equation for the work done in an adiabatic process simplifies to

$$w = C_V(T_f - T_i) = C_V \Delta T \quad (3.3.9)$$

Now we'll consider the heat flow during one of these processes: For an adiabatic process,  $dq = 0$  and so there is no heat flow! Then, the change in internal energy is given solely by the work done during the transformation:

$$\Delta U = w = C_V \Delta T \quad (3.3.10)$$

## 3.4 Heat Engines

An engine is simply a device that uses a cycle to convert energy from one form to another and always returns to its original state once the process is complete. In particular, a heat engine is one that receives heat ( $q_{in}$ ) from a hot thermal reservoir and converts some of it into mechanical work. As we'll see, in reality it is impossible to convert all of this heat into mechanical work (this is the Kelvin Statement). Since not all of this heat is transformed into work, some of it must be lost to the surroundings ( $q_{out}$ ).

### 3.4.1 The Carnot Engine

The Carnot engine is a theoretical ideal thermodynamic cycle and provides an upper limit on the efficiency of any classical thermodynamic heat engine. A *major* consideration to make about the Carnot cycle is that it is purely theoretical. Not only do we assume perfectly reversible reactions but also ideal gasses.

With this in mind (and the first law of thermodynamics, as always), when considering a heat engine we see that all of the heat received by an engine ( $q_{in}$ ) cannot be converted into work ( $w_{out}$ ) while some of it is lost as heat.

In an analysis of engines it is useful to define the *efficiency* of an engine,  $\varepsilon$

$$\varepsilon = \frac{w_{out}}{q_{in}} = \frac{q_{in} - q_{out}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}} \quad (3.4.1)$$

The Carnot cycle is defined by 4 particular transformations of an ideal gas:

1. Reversible *isothermal* expansion at a hot temperature ( $T_h$ )
2. Reversible *adiabatic* expansion to a cold temperature ( $T_c$ )
3. Reversible *isothermal* compression to a hot temperature ( $T_h$ )
4. Reversible *adiabatic* compression to a cold temperature ( $T_c$ )

The fourth step completes the cycle, returning the engine to its initial state. We'll analyze the heat and work flow in each of these steps. Note that for all of these steps,  $q_{in}$  refers to the heat absorbed by the engine from the thermal reservoir and  $q_{out}$  refers to the heat extracted from the engine and released into the surroundings (typically this is a cooling rod or some other very cold substance). Similarly,  $w_{in}$  refers to the work done on the engine and  $w_{out}$  refers to the work the engine does on its surroundings. Additionally, I'll refer to the hot temperature of the thermal reservoir as  $T_h$  and the colder temperature as  $T_c$ .

#### 1. Reversible Isothermal Expansion from Hot to Hot

For an isothermal expansion we can compute the work easily:

$$w_{in} = -w_{out} = - \int P dV = - \int_{V_i}^{V_f} \frac{nRT_h}{V} dV = -nRT_h \ln \left( \frac{V_f}{V_i} \right)$$

Thus, we see that the work output by the engine in the first step is

$$w_{out} = nRT_h \ln \left( \frac{V_f}{V_i} \right)$$

In the isothermal expansion of an ideal gas  $\Delta U = 0$  so by the First Law of Thermodynamics we have  $q_{out} = -w_{out}$  so that  $q_{in} = w_{out}$  and we can express the heat absorbed by the system as

$$q_{in} = w_{out} = nRT_h \ln \left( \frac{V_f}{V_i} \right)$$

#### 2. Reversible Adiabatic Expansion from Hot to Cold

In an adiabatic expansion we have  $dq = 0$  and so by the First Law of Thermodynamics we have  $dU = dw$  and we can compute the work done by the engine as

$$w_{out} = -w_{in} = - \int_{T_i}^{T_f} C_V dT = -C_V(T_c - T_h) = C_V(T_h - T_c)$$

Notice that we assume there is no dependence on temperature for the heat capacity because the Carnot cycle is interested in ideal gasses.

#### 3. Reversible Isothermal Compression from Cold to Cold

Similar to above, we can compute the work performed by the engine on the surroundings in an isothermal expansion as

$$w_{out} = -w_{in} = \int P dV = - \int_{V_i}^{V_f} \frac{nRT_c}{V} dV = -nRT_c \ln \left( \frac{V_f}{V_i} \right)$$

Moreover, since this is an isothermal process we have that  $\Delta U = 0$  and so  $q_{in} = w_{out}$ .

#### 4. Reversible Adiabatic Compression from Cold to Hot

Again, a pretty straightforward calculation considering we did it a second ago

$$w_{out} = - \int dU = - \int_{T_i}^{T_f} C_V dT = -C_V(T_c - T_h) = C_V(T_h - T_c)$$

Make sure to remember that for any adiabatic process,  $dq = 0$ .

We can now summarize our results in the following table, using the preceding diagram as reference points for the processes as well as the initial and final volumes for each process:

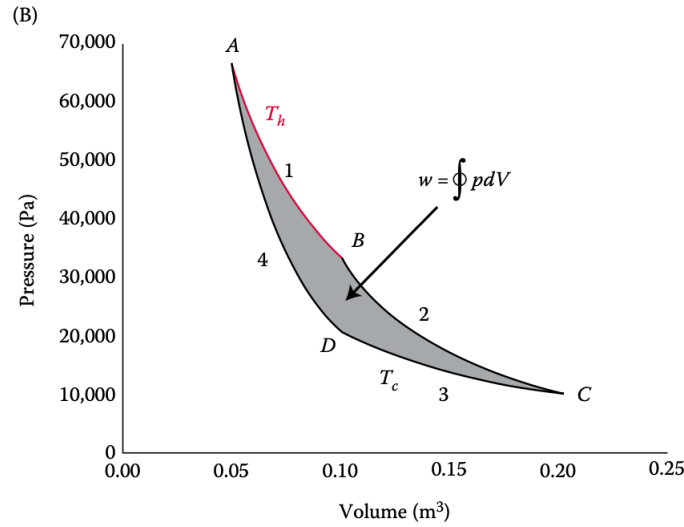


Figure 3.1: The Carnot Cycle. The shaded region represents the total work done on the surroundings during the transformation

Heat and Work for each Process of the Carnot Cycle		
Process	Heat Flow into Engine	Work Done by Engine
Isothermal Expansion	$q_1 = q_{in} = nRT_h \ln \left( \frac{V_B}{V_A} \right)$	$nRT_h \ln \left( \frac{V_B}{V_A} \right)$
Adiabatic Expansion	0	$C_V(T_c - T_h)$
Isothermal Compression	$q_3 = -q_{out} = nRT_c \ln \left( \frac{V_D}{V_C} \right)$	$nRT_c \ln \left( \frac{V_D}{V_C} \right)$
Adiabatic Compression	0	$C_V(T_h - T_c)$

Recall our expression for the efficiency of a heat engine, Equation (3.4.1). Using this, we can express  $q_{out}$  and  $q_{in}$  in terms of the quantities above, i.e., the initial and final temperatures and volumes:

$$\varepsilon = 1 - \frac{-nRT_c \ln(V_D/V_C)}{nRT_h \ln(V_B/V_A)} = 1 - \frac{nRT_c \ln(V_C/V_D)}{nRT_h \ln(V_B/V_A)} \quad (3.4.2)$$

In order to simplify this expression recall that for adiabatic processes,  $PV^\gamma = \text{constant}$  and so

$$\begin{aligned} P_B V_B^\gamma &= P_C V_C^\gamma \\ \frac{nRT_h}{V_B} V_B^\gamma &= \frac{nRT_c}{V_C} V_C^\gamma \\ T_h V_B^{\gamma-1} &= T_c V_C^{\gamma-1} \\ \frac{T_h}{T_c} &= \left( \frac{V_C}{V_B} \right)^{\gamma-1} \end{aligned}$$

for the isothermal compression of the gas, and

$$\begin{aligned} P_D V_D^\gamma &= P_A V_A^\gamma \\ \frac{nRT_c}{V_D} V_D^\gamma &= \frac{nRT_h}{V_A} V_A^\gamma \\ T_c V_D^{\gamma-1} &= T_h V_A^{\gamma-1} \\ \frac{T_h}{T_c} &= \left( \frac{V_D}{V_A} \right)^{\gamma-1} \end{aligned}$$

which implies that

$$\begin{aligned} \left( \frac{V_D}{V_A} \right)^{\gamma-1} &= \left( \frac{V_C}{V_B} \right)^{\gamma-1} \\ \frac{V_B}{V_A} &= \frac{V_C}{V_D} \end{aligned}$$

Consequently, we can substitute into Equation (3.4.2) to afford

$$\varepsilon = 1 - \frac{nRT_c \ln(V_B/V_A)}{nRT_h \ln(V_B/V_A)} = 1 - \frac{T_c}{T_h} \quad (3.4.3)$$

Eureka! This short equation implies that the primary constraint on an engine's efficiency is how cold the cold reservoir is. Moreover, the only point at which an engine could be 100% efficient is at *absolute zero*.

Another way of looking at the maximum work output of a Carnot engine is to consider the processes which do the work, that is, the isotherms. Ideally, the isothermal expansion is at a high temperature, thereby maximizing the area under the curve in the  $PV$  diagram. Additionally we would want the adiabatic expansion to reach the largest volume possible, thereby increasing the area under the curve in the  $PV$  diagram again. A large as possible volume increase during the adiabatic expansion also minimizes the area under the curve during the isothermal compression, which *decreases* the area under the curve in the  $PV$  diagram but since it is a compression this would be favorable. The below diagram illustrates these “optimized” transformations.

The following table summarizes everything we would ever really need to know about the Carnot cycle. Make sure to note the use of  $q_{in}$  and  $w_{out}$  for the engine instead of the typical  $q$  and  $w$  used to represent the heat absorbed by and work done on the system, respectively.

Heat, Work, and $\Delta U$ for the Reversible Carnot Cycle					
Segment	Initial State	Final State	$q_{in}$	$w_{out}$	$\Delta U$
$A \rightarrow B$	$P_A, V_A, T_{hot}$	$P_B, V_B, T_{hot}$	$q_{in,AB} > 0$	$w_{out,AB} > 0$	0
$B \rightarrow C$	$P_B, V_B, T_{hot}$	$P_C, V_C, T_{cold}$	0	$w_{out,BC} > 0$	$w_{out}$
$C \rightarrow D$	$P_C, V_C, T_{cold}$	$P_D, V_D, T_{cold}$	$q_{in,CD} < 0$	$w_{out,CD} < 0$	0
$D \rightarrow A$	$P_D, V_D, T_{cold}$	$P_A, V_A, T_{hot}$	0	$w_{out,DA} < 0$	$w_{out}$
Cycle	$P_A, V_A, T_{hot}$	$P_A, V_A, T_{hot}$	$\sum q_{in}$	$\sum w_{out}$	0

Ultimately, the reversible Carnot engine acts as an upper limit on efficiency, as stated in the “*Carnot Theorem*”:

No heat engine operating between two temperatures can be more efficient than a reversible Carnot engine operating between the same two temperatures.

Expressing the Carnot Theorem in terms of efficiencies,

$$\begin{aligned}\varepsilon_{rev} &> \varepsilon_{irr} \\ 1 - \frac{T_{rev}}{T_h} &> 1 - \frac{q_{out,irr}}{q_{in,irr}} \\ \frac{T_{rev}}{T_h} &< \frac{q_{out,irr}}{q_{in,irr}}\end{aligned}\tag{3.4.4}$$

The subscripts *rev* and *irr* refer to reversible and irreversible cycles, respectively. Note that the left-hand side of the inequality can be used because the temperature of a reversible Carnot engine is well defined throughout the cycle. Although this is not the case for irreversible cycles, the heat flow is still well defined and can be used on the right-hand side of the inequality. Rearranging Equation (3.4.4) gives

$$\frac{q_{in,irr}}{T_h} - \frac{q_{out,irr}}{T_c} < 0$$

where  $q_{out} = -q_{in}$  for the Carnot engine. Then, if we use this idealized limit of  $q_{out} = -q_{in}$ , we have

$$\frac{q_{in,irr}}{T_h} + \frac{q_{in,irr}}{T_c} \leq 0$$

for an irreversible process. In approximating an irreversible heat engine, we can use a collection of reversible Carnot cycles so that the above inequality can be rewritten as

$$\sum_{i=1}^n \frac{q_i}{T_i} < 0$$

and in the limit as  $n \rightarrow \infty$ ,

$$\oint_{irr} \frac{dq_{irr}}{T} < 0\tag{3.4.5}$$

Here, it is worth remembering that  $dq_{irr}$  represents the heat *absorbed* by the engine. Since this quantity is less than zero we observe that for an irreversible heat engine, some of the heat must be lost and therefore not all of it can be converted to work (which agrees with everything we've said up until this point).

Regardless of whether or not the cycle is reversible, if the engine is returned to its original state then all of the state functions must remain unchanged (i.e.,  $\Delta S = 0$ ).

How can we relate the macroscopic, idealized example of the Carnot engine back to a microscopic model? Well, we already know that heat and work are both ways to change the internal energy of a gas. In contrast to heat, work can be thought of as *organized* energy, e.g., for a gas to do work on a piston the molecules must all move in the same direction (against the piston). On the other hand, heat is much more like *random* energy, that is, there is no requirement for what direction the molecules must move or behave in order to absorb heat. All that is required when heat is absorbed is for the kinetic energy of the particles to increase (for idealized gasses, all of the internal energy is in the form of kinetic energy). Hence, there are fewer arrangements of particles in a gas that “look” like work, thereby favoring heat.

Let's return to the Carnot cycle. Notice that if we sum  $q$  across all of the processes in the cycle,  $\sum q \neq 0$  (this makes sense because heat is not a state function). However, recall from above that

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Using a little bit of algebraic gymnastics we can rewrite this as

$$\ln\left(\frac{V_B}{V_A}\right) = -\ln\left(\frac{V_D}{V_C}\right)\tag{3.4.6}$$

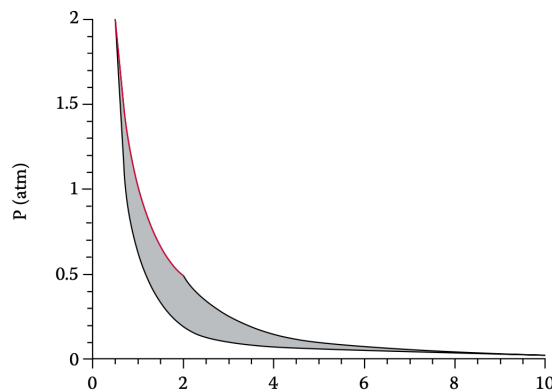


Figure 3.2: In the first isothermal expansion step, the initial hot temperature is maximized and in the succeeding adiabatic expansion the final volume reached is also maximized. Both of these conditions maximize the area under the curve, thereby maximizing the work done by the engine on the surroundings.

and take the sum of the heat across the entire cycle to afford the following result:

$$\begin{aligned}
 q_{in} + q_{out} &= nRT_h \ln \left( \frac{V_B}{V_A} \right) + nRT_c \ln \left( \frac{V_D}{V_C} \right) \\
 &= nRT_h \ln \left( \frac{V_B}{V_A} \right) - nRT_c \ln \left( \frac{V_B}{V_A} \right) \\
 &= (T_h - T_c)nR \ln \left( \frac{V_B}{V_A} \right)
 \end{aligned}$$

Thus, we see that if we define a new quantity  $q/T$  it would be zero over the entire cycle. In other words, the quantity  $q/T$  acts like a *state function*<sup>2</sup>. Thus,

$$\oint \frac{dq_{rev}}{T} = 0 \quad (3.4.7)$$

which implies that  $dq_{rev}/T$  acts like an exact differential. We refer to this state function as the *entropy*,

$$dS = \frac{dq_{rev}}{T} \quad (3.4.8)$$

This is another way of coming across an expression for the entropy as its defined in Sections ?? and ??

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<sup>2</sup>It's important to note that this result holds *only if the cycle is reversible*. Had any step been irreversible we cannot define this state function. Recall that  $q_{rev} > q_{irrev}$ .

## CHAPTER

# 4

# CHEMICAL POTENTIAL

*Chemical potential.*

- *Scientist*

In developing a robust analysis of thermodynamic systems we need to begin to consider the concentrations of different chemical components involved in a reaction. In particular, elucidating the thermodynamic contributions from each species, that is, how chemical  $i$  effects the enthalpy, entropy, and Gibbs free energy change of a reaction, for example. This foundational approach will offer a basis for analyzing simple reactions and phase transitions, as well as additional Maxwell relations that offer a framework for energetic coupling.

Firstly, we'll consider the idea of *partial molar quantities*, an approach to separating thermodynamic contributions from each species that does not require detailed structural knowledge of the chemical species or their modes of interaction. Next, the idea of a *chemical potential* will be developed as a means of predicting the phase of a species which will prevail at equilibrium for different thermodynamic systems. The chemical potential will be applied to systems with phase transitions and chemical reactions and ultimately afford the foundation for which we can analyze phase transitions using the *Clausius-Clapeyron equation*.

## 4.1 Partial Molar Quantities

A partial molar quantity is the amount of a particular extensive thermodynamic quantity contributed per mole of a substance. Such a quantity is represented as  $\tilde{X}_i$  where the bar refers to “per mole” and the subscript  $i$  denotes the particular species in question.

An important distinction that's made when converting to partial molar quantities is that whereas  $X_i$  is extensive,  $\tilde{X}_i$  is intensive. Intensive properties of a system typically provide a more fundamental description of a thermodynamic system than do their extensive counterparts (for example, consider the enthalpy of a reaction versus the molar enthalpy. Clearly, one is more illustrative of the chemistry going on than the other).

We'll begin our analysis of partial molar quantities by considering the partial molar volume(s) of a system because it closely parallels the behavior and intuition behind the partial molar Gibbs energy, a measurement that will be of immense use to us.

### 4.1.1 Partial Molar Volume

The partial molar volume of a system is defined as

$$\tilde{V}_i = \frac{V_i}{n_i} \quad (4.1.1)$$

where  $n_i$  is the number of moles of chemical  $i$  and  $V_i$  is the volume assumed by the same chemical. For single-species systems, this equation simplifies as  $\tilde{V}_i^* = V/n_i$  where  $\tilde{V}_i^*$  is used to denote the fact that the system is composed of only one species (we'll be interested in single-species systems for the majority of this beginning part). Rearranging Equation (4.1.1) affords

$$V = \tilde{V}_i^* n_i$$

This simple rearrangement better illustrates the fact that  $\tilde{V}$  acts as a proportionality constant, relating how the volume contributed by a particular species in a reaction changes with the number of moles of the species. In particular, if we consider incredibly small incremental changes in  $n_i$  we see that the partial molar volume is in fact a partial derivative:

$$\tilde{V}_i = \left( \frac{\partial V_i}{\partial n_i} \right)_{P,T,n_{i \neq j}} \quad (4.1.2)$$

The subscripts of the partial derivative indicate that pressure and temperature are being held constant, in addition to the number of moles of the other species involved in the reaction. Finally, we see that the total volume differential can be expressed in the following form for a chemical reaction with a single species:

$$dV = \tilde{V}_i^* n_i = \left( \frac{\partial V}{\partial n_i} \right) dn_i \quad (4.1.3)$$

Now we'll move on to multiple component systems. Consider a 1:1 mixture of water and ethanol so that the mole fractions are  $x_{\text{H}_2\text{O}} = x_{\text{EtOH}} = 0.5$ . In mixing 50 mL of water with 50 mL of ethanol, we afford a mixed solution totaling 97 mL, in contrast to the case using *just* pure water. I don't yet know why this happens, it's known as "mixing volume ideality", but I'm dying to find a physical explanation. Nevertheless, this discrepancy reflects the dependence of partial molar volumes on composition. In fact, we can represent the total molar volume of an ideal solution (for two components water and ethanol, this case) as

$$\tilde{V} = x_{\text{H}_2\text{O}} \tilde{V}_{\text{H}_2\text{O}}^* + x_{\text{EtOH}} \tilde{V}_{\text{EtOH}}^* \quad (4.1.4)$$

The use of the star in this equation illustrates the fact that in order for this equality to hold we assume ideality. In fact, multiplying this equation by the total number of moles in solution affords the sensible result,

$$V = n_{\text{H}_2\text{O}} \tilde{V}_{\text{H}_2\text{O}} + n_{\text{EtOH}} \tilde{V}_{\text{EtOH}} \quad (4.1.5)$$

Unsurprisingly, this equation generalizes to any number of species with ease. More generally, we can also express the total partial derivative of the volume of this sort of solution as

$$dV = \left( \frac{\partial V}{\partial n_A} \right)_{n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{n_A} dn_B \quad (4.1.6)$$

which generalizes similarly.



### 4.1.2 Partial Molar Gibbs Energy

The partial molar Gibbs free energy is defined exactly as we'd expect. Because of its importance, however, its given the special denomination of “chemical potential”:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{n_{i \neq j}} \quad (4.1.7)$$

The chemical potential can be thought of as an analogue to potentials in physics, such as the electric potential or gravitational potential; particles of a substance tend to move from high chemical potential to low potential. The chemical potential has applications in a nearly inappropriate amount of disciplines. An understanding in everything from chromatography to electrochemistry<sup>1</sup> benefits from having a foundational understanding of the chemical potential. Something I recently just learned about are *theoretical plates*, the hypothetical stage in a chromatographic process in which the liquid and vapor phases of a substance are in equilibrium. The performance of a separation process such as chromatography depends on having a series of these theoretical plates. Alright that was only a small tangent back to the things that we'll be tested on at one point.

Before diving into a derivation and analysis of the relationships between some thermodynamic quantities and the chemical potential, it would behoove us not to mention the close (and ideally helpful) analogies between the chemical potential, temperature, and pressure, three intensive variables which may determine the equilibrium of a system:

1. *Temperature* determines equilibrium with respect to heat flow. Heat flows from higher temperatures to lower ones (a restatement of the second law). When flow stops, equilibrium is attained and the temperature is uniform.
2. *Pressure* determines the equilibrium of a system with respect to volume change. When a higher-pressure part of the system expands at the expense of one at a lower pressure, this can be considered a “flow” of volume from low pressure to high pressure. When flow stops, equilibrium is attained and pressure is uniform<sup>2</sup>.
3. *Chemical potential* determines the equilibrium with respect to the flow of matter. Each species of matter flows from high chemical potential to low chemical potential. When the flow stops, equilibrium is attained and the chemical potential of each species is uniform.

If variations in temperature and pressure are considered alongside variations in the number of moles of each species, the chemical potentials combine nicely to afford the total partial differential of Gibbs free energy as

$$dG = VdP - SdT + \sum_{i=1} \mu_i dn_i \quad (4.1.8)$$

where the summation on the right iterates through every chemical species involved in the reaction. This variation equation offers a number of additional Maxwell relations. Moreover, this new equation for the Gibbs free energy will be paramount for systems with phase transitions, chemical reactions, or that are open and can exchange matter with the surroundings (all of these types of transformations can lead to changes in  $n$ ).

This affords a new expression for the total partial differential of  $dG$ :

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_i, n_j} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_i, n_j} dP + \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_i} dn_i + \left( \frac{\partial G}{\partial n_j} \right)_{T, P, n_j} dn_j \quad (4.1.9)$$

Note that we've already named all of these quantities:

$$dG = -SdT + VdP + \mu_i dn_i + \mu_j dn_j \quad (4.1.10)$$

<sup>1</sup>Depending on how much chemistry you're familiar with that may or may not be a large breadth of knowledge.

<sup>2</sup>This realization of the pressure for a system must be modified if such effects as gravity are significant.

Hold on a minute! Above we just defined the molar Gibbs free energy *as the sum of the chemical potential* so it can be expressed as

$$\tilde{G} = \mu_i + \mu_j \Leftrightarrow G = n_i\mu_i + n_j\mu_j \quad (4.1.11)$$

which means we should also be able to express the differential Gibbs free energy as

$$dG = d\mu_i n_i + \mu_i dn_i + d\mu_j n_j + \mu_j dn_j \quad (4.1.12)$$

At this point, we're left with two equations expressing the same quantity:

$$\begin{aligned} dG &= -SdT + VdP + \mu_i dn_i + \mu_j dn_j \\ dG &= d\mu_i n_i + \mu_i dn_i + d\mu_j n_j + \mu_j dn_j \end{aligned}$$

Putting these together affords the following relationship:

$$d\mu_i n_i + d\mu_j n_j = SdT + VdP$$

We can generalize this equation to any number of chemical species nicely, affording what's known as the *Gibbs-Duhem equation*:

$$\sum_{i=1}^n n_i d\mu_i = -SdT + VdP \quad (4.1.13)$$

Essentially, this equation is telling us that the chemical potentials for each species in a reaction *are dependent on one another*. For a single species this equation simplifies as

$$nd\mu = -SdT + VdP \Leftrightarrow d\mu = -\tilde{S}dT + \tilde{V}dP$$

Up until this point we've talked all about Gibbs free energy. How might chemical potential be expressed in terms of other state functions such as the Helmholtz free energy of a system or the internal energy? (An excellent question, might I add). Well, let's consider the Helmholtz free energy as an example: We can express the Helmholtz free energy as

$$A = U - TS + \sum_{i=1}^n \mu_i n_i$$

for a reaction with  $n$  chemical species present. Then, the total partial differential of  $A$  can be computed as

$$dA = PdV - SdT + \sum_{i=1}^n \mu_i dn_i$$

recalling the derivation for the total partial differential of the Helmholtz free energy from Section ?? and adding in the term(s) for the influence of the chemical potential. Using the same equation for the total partial differential of the Helmholtz energy, we see that

$$\mu_i = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_{i \neq j}} \quad (4.1.14)$$

Hopefully it's clear that a similar relationship will appear for the internal energy of a system as well as the enthalpy. I'll leave those derivations to you because I don't wanna do it. Here they all are:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_{i \neq j}} = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_{i \neq j}} = \left( \frac{\partial H}{\partial n_i} \right)_{T, P, n_{i \neq j}} = \left( \frac{\partial U}{\partial n_i} \right)_{S, V, n_{i \neq j}}$$

One important aspect of these relationships is that the partial derivatives are all taken while the respective

*natural variables* are held constant.

Let's keep in mind the intuition behind defining a chemical potential in the first place: The notion of  $\mu$  helps us predict the spontaneity of a process that involves adding or taking away molecular components of a transformation. This includes both chemical transformations where multiple species are present and phase transitions where only a single chemical is present but in different phases. This statement begs an important question: How do we define a phase? Typically we define three phases of matter, solid, liquid, and gas. However, phases and phase transitions encompass a much broader range of physical phenomena. A quick example might be *magnetism*, the uniform orientation of electron spins within a material. Another example might be the *mesophase* of a substance, a state of matter in between a liquid and a solid. Some examples of mesophases include the lipid bilayers of cell membranes and gelatin. In the next section we'll take a more rigorous approach to defining the properties of a thermodynamic phase.

One thing that sometimes peeves me in this class is the lack of formalized math and statistics that's applied to some of these complicated systems. Old whites dudes have been grinding for years to provide rigorous definitions for everything we've talked about and will talk about, but for the sake of "simplicity" they're just ignored for the most part. That's my short preface into trying to reintroduce the use of partial derivatives for important thermodynamic relationships.

Recall that through the use of the total partial differential for Gibbs free energy we have the relationship

$$-S = \left( \frac{\partial G}{\partial T} \right)_{P, n_i \neq j}$$

so that we can rewrite our definition for the Gibbs free energy as

$$G = H + T \left( \frac{\partial G}{\partial T} \right)_{P, n_i \neq j}$$

Differentiating with respect to an infinitesimal change in amount of substance  $i$ , we have that

$$\left( \frac{\partial G}{\partial n_i} \right)_{P, n_i \neq j} = \left( \frac{\partial H}{\partial n_i} \right)_{P, n_i \neq j} + T \left( \frac{\partial^2 G}{\partial n_i \partial T} \right)_{P, n_i \neq j} \quad (4.1.15)$$

As a result of Clairaut's theorem we can change the order of differentiation to afford an equivalent expression for the right-most partial derivative in the expression above,

$$\left( \frac{\partial^2 G}{\partial n_i \partial T} \right)_{P, n_i \neq j} = \left( \frac{\partial^2 G}{\partial T \partial n_i} \right)_{P, n_i \neq j} = \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_i \neq j}$$

ultimately lending itself to the expression

$$\mu_i = h_i + T \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_i \neq j} \quad (4.1.16)$$

where  $h_i$  is the partial molar enthalpy. This equation for the chemical potential will prove useful later when we consider ideal mixtures.

### 4.1.3 Consequences of an Ideal Solution

Just as the treatment of gasses can be simplified by starting with an idealized kind of gas, so can mixtures be simplified. However, this range of usefulness will prove much more restricted than the tried-and-true  $PV = nRT$ .

There are several equivalent ways of defining an ideal mixture. A common analytical definition is given by

$$\mu_i = \mu_i^* + RT \ln x_i \quad (4.1.17)$$

where  $\mu_i^*$  is the chemical potential of the pure liquid and  $x_i$  is the mole fraction of the compound in solution. As we'll come to realize, this equation affords an easy way of showing why the enthalpy of mixing for an ideal solution is necessarily zero (that time of realization is now, by the way). By the chain rule, we have that

$$\begin{aligned}\frac{\partial(\mu_i/T)}{\partial T} &= \frac{T \frac{\partial \mu_i}{\partial T} - \mu_i \frac{\partial T}{\partial T}}{T^2} \\ &= -\frac{1}{T} \frac{\partial \mu_i}{\partial T} - \frac{\mu_i}{T^2}\end{aligned}$$

so that we can make the substitution

$$-T^2 \frac{\partial(\mu_i/T)}{\partial T} = -T \frac{\partial \mu_i}{\partial T} + \mu_i$$

into Equation (4.1.16) to afford the following relationship:

$$h_i = -T^2 \left( \frac{\partial(\mu_i/T)}{\partial T} \right)_{P, n_i \neq j} \quad (4.1.18)$$

To prove the utility of our expression for the partial molar enthalpy above, we'll first rewrite Equation (4.1.17) by dividing through by temperature,

$$\frac{\mu_i}{T} = \frac{\mu_i^*}{T} + R \ln x_i \quad (4.1.19)$$

and differentiating this equation with respect to temperature (following the same logic using the chain rule a moment ago), followed by multiplying through by  $-T^2$ , we find that

$$h_i = h_i^* \quad (4.1.20)$$

That is to say, *the change in enthalpy of mixing for an ideal solution is zero.*

Using Equation (4.1.17) as a template, we could also define the chemical potential of a pure *vapor* as

$$\mu_i = \mu_i^\circ + RT \ln \left( \frac{P_i}{P^\circ} \right) \quad (4.1.21)$$

where the fraction  $P_i/P$  can be thought of as a “pressure fraction,” analogous to mole fractions in the case of the solution<sup>3</sup>. If the vapor is in equilibrium with its solution, the chemical potential of species  $i$  in either phase must be the same, so that

$$\mu_i^* = \mu_i^\circ + RT \ln \left( \frac{P_i^*}{P^\circ} \right)$$

Taking the difference between this equation and Equation (4.1.21), we find

$$\begin{aligned}\mu_i - \mu_i^* &= \mu_i^\circ + RT \ln \left( \frac{P_i}{P^\circ} \right) - \left[ \mu_i^\circ + RT \ln \left( \frac{P_i^*}{P^\circ} \right) \right] \\ &= RT \ln \left( \frac{P_i}{P^*} \right) \\ &= RT \ln x_i\end{aligned}$$

from which we see that  $P_i = x_i P_i^*$  also known as *Raoult's law*.

#### 4.1.4 Consequences of a Nonideal Solution

Solutions that behave truly ideal are few and far between and the relatively simple relationships derived in the preceding section are not nearly as applicable as we may like. Just as in the case of the nonideal gas, however,

<sup>3</sup>A more common expression for  $\mu_i$  of an ideal vapor defines the quantity in terms of *fugacity*, a property of a real gas which, when substituted for the partial pressure  $P_i$  of an ideal gas, gives equations applicable to a real gas. The fugacity is related to the real pressure of the gas through the relationship  $f = \varphi P$ , where  $\varphi$  is the *fugacity coefficient*.

using these equations as a template for defining relationships between the real quantities of a substance will prove beneficial. For a solution, we introduce the *activity*,  $a_i$ , that satisfies

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (4.1.22)$$

for each chemical in a solution. In order to define the standard chemical potential for a solution we'll need to first specify which substance will assume the role of our solvent. Then,  $\mu_i^\circ$  is the chemical potential of the pure solvent. For the other chemicals in solution, the reference state is defined such that  $[i] = 0$  M, i.e., the concentration is zero<sup>4</sup>. Then, the standard chemical potential is such that

$$\lim_{x_i \rightarrow 1} \frac{a_i}{x_i} = 1 \quad (4.1.23)$$

The ratio  $a_i/x_i$  is the *activity coefficient*, symbolized by  $\gamma_i$ .

## 4.2 Phases and Phase Transitions

Finally we'll determine the major incentive for defining the chemical potential: *At equilibrium, the phase of a substance with the lower chemical potential prevails.*

Familiar phases typically differ in the type and quantity of *non-covalent interactions between molecules*; Van der Waals forces and induced dipoles are good examples of these. Gases often have the fewest intermolecular interactions, then liquids, then solids. Compared to gases, liquids and solids have vastly more intermolecular interactions, however, the molecules in a liquid are *isotropically* (randomly) oriented so that there is no long-range order. Solids on the other hand do have long-range order, i.e., *crystallinity*.

Not all phases are distinguished by non-covalent interactions, though. Some differ in their covalent bonding pattern. For example take C(s). Carbon can exist as graphene, an  $sp^2$  hybridized form which exhibits aromaticity, and diamond, an  $sp^3$  hybridized form which forms a strong covalent network where each carbon is bound to four other carbons.

Usually we can distinguish between which phase of a substance is favored at or around standard conditions. At room temperature water will be liquid and we can freeze or it boil it by dropping it below  $0^\circ\text{C}$  or brining it above  $100^\circ\text{C}$ , respectively. However, which phase of water will be favored at  $75^\circ\text{C}$  and 15 atm? Here we can invoke the chemical potential.

Let  $\alpha$  and  $\beta$  represent different phases of a component (for example, the liquid and vapor phases of water). We can write down a change in Gibbs free energy in response to the change in the number of moles of each phase:

$$dG = \mu^\alpha dn^\alpha + \mu^\beta dn^\beta$$

By the conservation of matter it must be the case that  $dn^\alpha = -dn^\beta$  so that we can rewrite this as

$$dG = (\mu^\alpha - \mu^\beta)dn^\alpha$$

The above expression makes the following claim clear: Under conditions where  $\mu^\alpha < \mu^\beta$ , at equilibrium the system will consist entirely of the  $\alpha$  phase because the partial molar Gibbs free energy with respect to the  $\alpha$  phase will be negative, indicating the direction of the reaction which minimizes  $G$ .

In contrast, the point where  $\mu^\alpha = \mu^\beta$ , i.e.,  $dG = 0$ , the equilibrium condition is maintained regardless of the change in moles of phase  $\alpha$  and so both phases can exist in equilibrium. We call this point *phase coexistence*. Another way of thinking about phase coexistence is that the material can change reversibly between phases.

Thus, we're left with the result that if we can compute the chemical potential of different phases at any condition we will know which phase prevails at that condition (at equilibrium). So, let's try and do that

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<sup>4</sup>This condition is sometimes also referred to as the *state of infinite dilution*.

Starting from Equation (4.1.11) for a single species we have that

$$\mu^\alpha = \tilde{G}^\alpha = \tilde{H}^\alpha - T\tilde{S}^\alpha \quad (4.2.1)$$

for some phase  $\alpha$ . As a minor aside, notice that this equation explains the two familiar phase changes of water. Consider the differential chemical potential:

$$d\mu^\alpha = d\tilde{G}^\alpha = -\tilde{S}^\alpha dT + \tilde{V}^\alpha dP \quad (4.2.2)$$

As the temperature of the sample increases, the Gibbs free energy will decrease (because of the negative sign associated with that term) and so the phase with a greater entropy will be favored (explaining the transition from solid to liquid to gas as temperature increases). Returning to Equation (4.2.1), our goal now is to try and express  $\mu^\alpha$  in terms of manipulable thermodynamic properties, e.g. temperature and pressure.

Recall that our key expressions for enthalpy and entropy in terms of pressure and temperature are in terms of the heat capacity,

$$\begin{aligned} dH = C_P dT &\Leftrightarrow H(T) = \int_{T_0}^{T_f} C_P(T) dT + H_r \\ dS = \frac{C_P}{T} dT &\Leftrightarrow S(T) = \int_{T_0}^{T_f} \frac{C_P(T)}{T} dT + S_r \end{aligned} \quad (4.2.3)$$

where  $H_r$  and  $S_r$  are reference states for the enthalpy and entropy, respectively. With these expressions we can evaluate the enthalpy and entropy changes over a temperature range with no phase change. *During* a phase change, however, none of the heat goes into changing the temperature of a substance and therefore the heat capacity is no good. Hence, we need a new quantity to define the energy change associated with phase change.

This new quantity is the *enthalpy of melting/vaporization/fusion etc.*, denoted  $\Delta\tilde{H}_m$ . Intuitively, the enthalpy of vaporization represents the heat being put into breaking up intermolecular reactions (thereby increasing potential energy) as opposed to speeding up molecules (which would have increased the kinetic energy of a sample). The *entropy of melting/vaporization/fusion etc.*, is defined how we might expect, as  $\Delta\tilde{S}_m = \Delta\tilde{H}_m/T_m$  where  $T_m$  represents the temperature at which the phase change occurs.

The last thing we need to define the chemical potential of a phase at a particular thermodynamic state is *reference states for enthalpy and entropy*, to define an absolute scale (recall from Equations (4.2.3) that when integrating we are left with reference enthalpies and entropies).

For enthalpy, this is an intrinsically arbitrary question: Which energy are we counting? We could be referencing the bond enthalpies of a compound, the energies of the intermolecular interactions between molecules of a compound, or even the electronic energy associated with the energies of electrons. Hence, we define the arbitrary reference point of 0 (enthalpy units, I suppose) to quantify the partial molar enthalpy of a phase transition as follows:

$$\tilde{H}(T) = 0 + \int_0^{T_m} \tilde{C}_P(T) dT + \Delta\tilde{H}_m + \int_{T_m}^{T_v} \tilde{C}_P(T) dT + \Delta\tilde{H}_v + \int_{T_v}^{T_f} \tilde{C}_P(T) dT \quad (4.2.4)$$

In contrast to enthalpy we do in fact have the ability to create an absolute reference point for the entropy. Because of its microscopic definition,  $S = k_B \ln W$ , at absolute zero a substance will have only one microstate<sup>5</sup>, that is, a perfectly crystalline structure. Hence,  $W = 1$  and therefore  $S = 0$ . This is known as the *third law of thermodynamics*. Now, we can define the partial molar entropy for a phase transition absolutely:

$$\tilde{S}(T) = 0 + \int_0^{T_m} \frac{\tilde{C}_P(T)}{T} dT + \Delta\tilde{S}_m + \int_{T_m}^{T_v} \frac{\tilde{C}_P(T)}{T} dT + \Delta\tilde{S}_v + \int_{T_v}^{T_f} \frac{\tilde{C}_P(T)}{T} dT \quad (4.2.5)$$

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<sup>5</sup>At absolute zero the number of *degenerate ground states* for a substance is incredibly small such that the *residual entropy* can be safely approximated as 0.

Ultimately, these equations will help us to do is derive a pressure-dependence for the chemical potential.

Recall Equation (4.2.2), relating the change in chemical potential of a phase to the natural variables of the Gibbs free energy,

$$d\mu^\alpha = -\tilde{S}^\alpha dT + \tilde{V}^\alpha dP \quad (4.2.6)$$

As discussed previously, the temperature dependence of this equation makes sense; as temperature increases the phase which maximizes entropy will be favored. What about the pressure dependence on the thermodynamic favorability of a phase? Funny you should ask because that's what I was just about to talk about.

As we can see from the Equation (4.2.6), phases with *large molar volumes* will have chemical potentials which vary (potentially significantly) with pressure. For all intents and purposes, the chemical potential of the condensed phases don't vary significantly with the pressure<sup>6</sup> and so we'll only consider the pressure-dependence of the chemical potential on the gaseous state. Suppose we consider a constant-temperature gas phase  $\alpha$  with chemical potential given by

$$d\mu^\alpha = \tilde{V} dP = \frac{RT}{P} dP$$

where we estimate the gas to be ideal and the  $n$  term drops out because the chemical potential is a molar quantity (by definition). Proceeding with integration:

$$\begin{aligned} \int_{P_r}^P d\mu^\alpha &= RT \int_{P_r}^P \frac{dP}{P} \\ \mu^\alpha(P) - \mu^\alpha(P_r) &= RT \ln \left( \frac{P}{P_r} \right) \\ \mu^\alpha(P) &= RT \ln \left( \frac{P}{P_r} \right) + \mu^\alpha(P_r) \end{aligned} \quad (4.2.7)$$

In the lecture slides Dr. Fried likes to use units of atm to simplify the logarithm in the final line. I will not do that. I refuse to be a slave to atm.

Now we're left with an expression for the chemical potential as a function of the pressure and temperature of the sample. Notice that  $\mu^\alpha(P_r)$  is a function of only temperature so that we can express it in terms of the enthalpy and entropy of the sample, with them as functions of temperature as well. Then, starting from Equation (4.2.7),<sup>7</sup>

$$\begin{aligned} \mu^\alpha(P, T) &= RT \ln \left( \frac{P}{P_r} \right) + \mu^\alpha(T; P_r) \\ &= RT \ln \left( \frac{P}{P_r} \right) + \tilde{H}^\alpha(T; P_r) - T\tilde{S}^\alpha(T; P_r) \\ &= RT \ln \left( \frac{P}{P_r} \right) + \tilde{H}_v^\alpha(; T_v, P_r) + \tilde{C}_P^\alpha(T - T_v) - T(\tilde{S}^\alpha(; T_v, P_r) + \tilde{C}_P^\alpha \ln(T/T_v)) \\ &= \tilde{H}_v^\alpha(; T_v, P_r) - T\tilde{S}^\alpha(; T_v, P_r) - \tilde{C}_P^\alpha T_v - T(R \ln(P/P_r) - \tilde{C}_P^\alpha + \tilde{C}_P^\alpha \ln(T/T_v)) \\ &= \mu^\alpha(; T_v, P_r) - \tilde{C}_P^\alpha T_v - T(R \ln(P/P_r) - \tilde{C}_P^\alpha(1 - \ln(T/T_v))) \end{aligned}$$

In the second line above I utilized Equations (4.2.4) and (4.2.5) to rewrite the enthalpies and entropies as they varied with temperature as the sum of reference enthalpies and entropies and their respective changes over a temperature range according to their dependence on the heat capacity. I colored them to try and make it more clear what was being substituted and moved around because I feel like the derivation provided in the slides does a poor job of this. Also in the last line I substituted

$$\mu^\alpha(; T_v, P_r) = \tilde{H}_v^\alpha(; T_v, P_r) - T\tilde{S}^\alpha(; T_v, P_r)$$

<sup>6</sup>At extreme pressures (we're talking on the order of gigapascals) solids undergo interesting pressure-dependent phase transitions. I think Dr. McQueen's lab might deal with pressures great enough to observe this.

<sup>7</sup>In the following expressions I've adopted the notation  $T(x; y)$  where  $T$  is a variable which varies with  $x$  with some constant parameter  $y$ .

by definition of the chemical potential for a phase.

At this point, I'm gonna stop doing math. We could try and simplify this further, however, we've reached a point where we can already draw some meaningful conclusions. Notice that everything on the right-hand side of the equation *varies only with pressure* for a fixed temperature. So, doing a tiny bit of analysis we find that *the chemical potential of the gaseous state increases as the pressure of the gas increases so that the gaseous state becomes less thermodynamically favorable*. I know, it was an annoying set of mathematical manipulations to get to an arguably underwhelming result. I agree.

So we've derived some sort of pressure dependence of the chemical potential for a sample and now we're left to determine how the pressure dependence changes with temperature and vice versa. Recall from looking at thermodynamic potentials that we utilized  $PV$  diagrams to visualize the properties of a thermodynamic system. Here, we'll follow a similar procedure to visualize phase changes, instead utilizing a  $PT$  diagram. Below is the  $PT$  diagram of water. There are a few labeled points: The *triple point* are the pressure and temperature conditions at which all three phases of matter exist in equilibrium. The *critical point* is the minimum pressure and temperature at which a substance can be distinguished between a gas and a liquid. In other words, beyond the critical point a substance can no longer be distinguished between the liquid and gas phases. Additionally, the triple point pressure corresponds to the minimum pressure at which the liquid phase of a substance can exist and the triple point temperature is *typically* the minimum temperature at which the liquid phase can exist<sup>8</sup>.

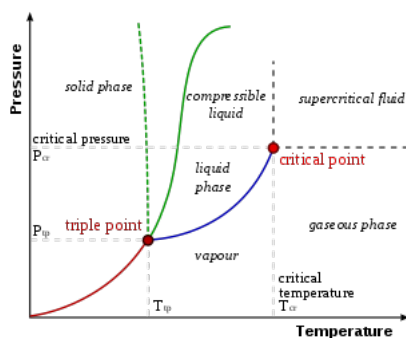


Figure 4.1: Phase diagram of water

Another major part of a phase diagram are the *coexistence curves*, the lines of the diagram on which neighboring phases can exist in equilibrium. The slopes of the coexistence curves are given by the *Clausius-Clapeyron equation*.

### 4.3 The Clausius-Clapeyron Equation

Although it's usually applied to liquid-vapor equilibrium, the Clausius-Clapeyron equation can be applied to a wide variety of circumstances: The conditions for validity are (1) it must involve equilibrium with respect to change that can take place reversibly at a constant temperature and pressure and (2) the equilibrium pressure must depend only on temperature.

As mentioned above, the slopes of the coexistence curves on a phase diagram are expressed by the *Clausius-Clapeyron equation*. So, consider the equilibrium of two phases, an  $\alpha$  and a  $\beta$  phase:

$$\mu^\alpha = \mu^\beta$$

Along a coexistence curve the chemical potential of a species will certainly change. Recall from the Gibbs-Duhem Equation (4.1.13) that the chemical potentials of the species in a thermodynamic system exhibit some dependence on the thermodynamic properties of that system. Hence, when the pressure and temperature of a

<sup>8</sup>One of the exceptions to this is water which has a coexistence curve between the gaseous and liquid phase with a negative slope.



sample change so will the chemical potentials. Along the coexistence curve, however, the change in potential will remain the same so that  $d\mu^\alpha = d\mu^\beta$  and we can express

$$-\tilde{S}^\alpha dT + \tilde{V}^\alpha dP = -\tilde{S}^\beta dT + \tilde{V}^\beta dP \quad (4.3.1)$$

by Gibbs-Duhem. A little bit of algebraic gymnastics gets us to the desired expression:

$$\begin{aligned} -\tilde{S}^\alpha dT + \tilde{V}^\alpha dP &= -\tilde{S}^\beta dT + \tilde{V}^\beta dP \\ (\tilde{V}^\beta - \tilde{V}^\alpha)dP &= (\tilde{S}^\beta - \tilde{S}^\alpha)dT \\ \frac{dP}{dT} &= \frac{\tilde{S}^\beta - \tilde{S}^\alpha}{\tilde{V}^\beta - \tilde{V}^\alpha} \end{aligned}$$

Which affords the Clausius-Clapeyron equation, defined as

$$\left(\frac{dP}{dT}\right)_{\alpha \rightarrow \beta} = \frac{\Delta\tilde{S}^{\alpha \rightarrow \beta}}{\Delta\tilde{V}^{\alpha \rightarrow \beta}} \quad (4.3.2)$$

where a substance is transitioning from the  $\alpha$  to the  $\beta$  phase. Clearly, since the entropy and volume change of a transition are not constant this slope will not be constant and we'd never expect the coexistence curve to be necessarily linear.

For most substances, we expect that the phase with a higher molar entropy ( $\tilde{S}_{gas} > \tilde{S}_{liquid} > \tilde{S}_{solid}$ ) will also have a higher molar volume ( $\tilde{V}_{gas} > \tilde{V}_{liquid} > \tilde{V}_{solid}$ ). Consequently, the slope of the coexistence curve is positive for almost all substances<sup>9</sup>

### 4.3.1 The Clapeyron Equation

The Clapeyron equation aims to approximate the thermodynamics of the liquid to gas phase transition for a substance. Beginning from Equation (4.3.2), we can approximate

$$\left(\frac{dP}{dT}\right)_{\alpha \rightarrow \beta} = \frac{\Delta\tilde{S}^{l \rightarrow g}}{\Delta\tilde{V}^{l \rightarrow g}} = \frac{\Delta\tilde{S}^{l \rightarrow g}}{\tilde{V}^g}$$

since the molar volume of the gaseous state will be far greater than that of the liquid phase. By the ideal gas law we can rewrite this as

$$\frac{\Delta\tilde{S}^{l \rightarrow g}}{\tilde{V}^g} = \frac{P\Delta\tilde{S}^{l \rightarrow g}}{RT}$$

and we can express the Clausius-Clapeyron equation as

$$\frac{dP}{P} = \left(\frac{\Delta\tilde{S}^{l \rightarrow g}}{R}\right) \frac{dT}{T} = \left(\frac{\Delta\tilde{H}_v}{R}\right) \frac{dT}{T^2}$$

where we took advantage of the fact that  $\Delta\tilde{S}^{l \rightarrow g} = \Delta\tilde{H}_v/T$ . Integrating this expression affords

$$\begin{aligned} \int_{P_r}^P \frac{dP}{P} &= \frac{\Delta\tilde{H}_v}{R} \int_{T_r}^T \frac{dT}{T^2} \\ \ln\left(\frac{P}{P_r}\right) &= \frac{-\Delta\tilde{H}_v}{R} \left(\frac{1}{T} - \frac{1}{T_r}\right) \end{aligned} \quad (4.3.3)$$

which is the *Clapeyron equation*.

The utility of the Clapeyron equation is in its ability to determine any point on a coexistence curve, *given we know at least one other point and the enthalpy of vaporization,  $\Delta\tilde{H}_v$* . But why the enthalpy of vaporization

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<sup>9</sup>Water is an excellent example of a substance with a negative slope for the coexistence curve for the liquid and solid phases. This is because the density of ice is *less than* the density of water, hence why ice floats on water! Ultimately this property is due in part to the strong hydrogen bonding water exhibits.

and not the enthalpy of fusion? Recall that the Clapeyron equation is an estimate for the liquid to gas phase transition. Thus, we're only interested in the enthalpy of vaporization.

Below is a birds-eye-view of what's been covered on phases so far:

1. A *phase* of a substance refers to a uniform macroscopic state characterized by certain types of interactions (enthalpy) and the substance's level of order (entropy). As a consequence, it will also be characterized by certain macroscopic properties (e.g., density, magnetism).
2. Phases can be characterized by an *order parameter*. Higher temperatures will favor the phase with lower order (gasses are favored over liquids, for example). The lower order phase typically has a lower enthalpy and higher entropy.

Now, here's an example problem utilizing (most) of what we talked about: The normal boiling point of benzene is 353.24 K and the vapor pressure of liquid benzene is 11.9 kPa at 298.15 K. The enthalpy of fusion is 9.95 kJ/mol and the vapor pressure of solid benzene is 137 Pa at 228.85 K. Firstly, compute  $\Delta\tilde{H}_v$ .

Notice that we have the following  $(P, T)$  pairs:

Phase	$P$ (kPa)	$T$ (K)
Liquid $\rightarrow$ Gas	101.325	353.24
Liquid	11.9	293.15
Solid	0.137	228.85

where the first coordinate was attained from the normal boiling point (normal implies atmospheric pressure), the second was given for the *liquid phase*, and the third was given for the *solid phase*. Then, the enthalpy of vaporization can be computed by the Clapeyron equation and the two  $(P, T)$  coordinates in the liquid phase:

$$\begin{aligned}\ln\left(\frac{101.325 \text{ kPa}}{11.9 \text{ kPa}}\right) &= \frac{-\Delta\tilde{H}_v}{R}\left(\frac{1}{353.24 \text{ K}} - \frac{1}{293.15 \text{ K}}\right) \\ \Delta\tilde{H}_v &= -R \ln\left(\frac{101.325 \text{ kPa}}{11.9 \text{ kPa}}\right)\left(\frac{1}{353.24 \text{ K}} - \frac{1}{293.15 \text{ K}}\right)^{-1} \\ &= 30.69 \text{ kJ/mol}\end{aligned}$$

Awesome!

Now compute  $\Delta\tilde{S}_v$ . This is far easier than above; all we have to do is divide the enthalpy of vaporization by the temperature of vaporization (which is given):

$$\Delta\tilde{S}_v = \frac{\Delta\tilde{H}_v}{T_v} = \frac{30.69 \text{ kJ/mol}}{353.24 \text{ K}} = 86.88 \text{ J/K/mol}$$

Amazing!

Lastly, find the triple point temperature and pressure for benzene. To compute the triple point we'll need to establish a system of 2 equations in 2 variables, those being the triple point temperature and triple point pressure. The two equations we'll use will consider as reference the points we're given on the coexistence curves and use the triple point parameters as the unknowns. The naive chemist may set this system up as follows:

$$\begin{aligned}\ln\left(\frac{P_{tp}}{11.9 \text{ kPa}}\right) &= -\frac{30.69 \text{ kJ/mol}}{R}\left(\frac{1}{T_{tp}} - \frac{1}{293.15 \text{ K}}\right) \\ \ln\left(\frac{P_{tp}}{0.137 \text{ kPa}}\right) &= -\frac{9.95 \text{ kJ/mol}}{R}\left(\frac{1}{T_{tp}} - \frac{1}{228.85 \text{ K}}\right)\end{aligned}$$

Why is this incorrect? Recall that the Clapeyron equation *is a model for transitions to the gaseous phase*. Hence, all of our equations should represent phase changes that evolve a gas. Notice that in the second equation which utilizes the enthalpy of *fusion* is illustrative of a transition from the solid to liquid phase. Instead of using the

enthalpy of fusion we need to find the enthalpy of sublimation which is representative of a phase transition from the solid to gaseous state. Since enthalpy is a state function this can be computed with ease:

$$\Delta\tilde{H}_{sub} = \Delta\tilde{H}_{vap} + \Delta\tilde{H}_{fus} = 40.64 \text{ kJ/mol}$$

Then, our system becomes

$$\begin{aligned}\ln\left(\frac{P_{tp}}{11.9 \text{ kPa}}\right) &= -\frac{30.69 \text{ kJ/mol}}{R}\left(\frac{1}{T_{tp}} - \frac{1}{293.15 \text{ K}}\right) \\ \ln\left(\frac{P_{tp}}{0.137 \text{ kPa}}\right) &= -\frac{40.64 \text{ kJ/mol}}{R}\left(\frac{1}{T_{tp}} - \frac{1}{228.85 \text{ K}}\right)\end{aligned}$$

which, following a little bit of algebraic gymnastics, affords the triple point temperature and pressures as  $P_{tp} = 5.97 \text{ kPa}$  and  $T_{tp} = 278 \text{ K}$ .

## 4.4 Gibbs Rule of Phase

*Gibbs rule of phase*, or just *the phase rule*, is a general principle governing  $PVT$  systems, that is, systems whose states are defined completely by pressure, volume, and temperature. The basis for this rule is that at equilibrium, the number of phases present places a constraint on the intensive variables. More rigorously, since the phases are in equilibrium with one another, the chemical potentials of the phases must be equal. Hence, a restriction is placed on one of  $P$ ,  $V$ , or  $T$  by the Gibbs-Duhem equation.

Let's motivate a mathematical definition by working up from a 1-component system. For a system of one phase, say, solid, assuming we do not allow for any phase transitions, we are free to vary any one of  $P$  or  $T$  without affecting the identity of the solid. By introducing a second phase, say, liquid, we've restricted our system to the coexistence curve between the solid and liquid phases so that if we choose to vary  $T$ ,  $P$  must also vary as to maintain the existence of both phases in equilibrium. Hence, we have one fewer *degree of freedom*. Naturally, at the triple point for a substance there are 0 degrees of freedom since the triple point is exactly that—a point. We could summarize the number of degrees of freedom  $F$  for this simple experiment as

$$F = 3 - \pi$$

where  $\pi$  is the number of phases of the substance present.

We could generalize our results to a system of multiple components with relative ease to afford the *Gibbs rule of phase*:

$$F = C - \pi + 2 \tag{4.4.1}$$

where  $F$  is the number of degrees of freedom a system has,  $\pi$  is the number of phases present, and  $C$  is the number of unique chemical species.<sup>10</sup>

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<sup>10</sup>Materials scientists oftentimes deal with phase changes between solid structures and therefore imagine pressure as being constant. This convention affords what is commonly referred to as the *condensed phase rule*, and is expressed as  $F = C - \pi + 1$ .

## CHAPTER

# 5

# CHEMICAL REACTIONS AND EQUILIBRIUM

### *Chemical Reactions*

- *Scientist*

Thermodynamics of mixing, connecting the macroscopic to the microscopic. Develop a theory of chemical equilibrium using potentials. Define some stuff.

The topic of “chemical reactions” is certainly a broad one: Everything ranging from why your apple rots when left out for too long to stars exploding in space can be considered a chemical reaction. Clearly, these two things are vastly different. One is the tragic destruction of something beautiful, the other has like a 0.000001% chance of affecting us cause stars are really far away. So, it’s important we define *standard states* for different chemical processes<sup>1</sup>.

A standard state is an *experimentally accessible reference state* for a thermodynamic quantity. Standard states are important because a multitude of thermodynamic quantities are easier to define *relative* to a standard state rather than being defined absolutely (consider the idea of trying to defining an absolute state for enthalpy as discussed in Section 4.2). We tackled this idea already a little bit with chemical potentials. Equation (4.2.7), for example, defines the chemical potential as a function of pressure given some reference pressure. Using the same equation as a motivating example, we can express the chemical potential for mixing two liquids together as

$$\mu_i^{soln} = \mu_i^* + RT \ln x_i \quad (5.0.1)$$

where  $\mu_i^{soln}$  is the chemical potential of species  $i$  in the mixture,  $\mu_i^*$  is the chemical potential of the pure liquid  $i$  with a mol fraction of 1, and  $x_i$  is the mole fraction of species  $i$ . We can express the potential for adding a solute to a solution analogously,

$$\mu_i^{soln} = \mu_i^\circ + RT \ln [i] \quad (5.0.2)$$

where  $\mu_i^\circ$  is the chemical potential of a solution with species  $i$  having a concentration of 1 M, and  $[i]$  is the concentration of species  $i$ .

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<sup>1</sup>One might think about how the standard states for the oxidation of an apple and a supernova differ.

## 5.1 The Thermodynamics of Mixing

As a simple model based off of the mixing discussed a moment ago, let's suppose we have a container of  $N$  lattice cells and we have  $N_p$  particles of species  $p$  and  $N_q$  particles of species  $q$  such that  $N_p + N_q = N$ . The maximum number of microstates associated with this system is given by the multinomial coefficient

$$W = \binom{N}{N_p, N_q} = \frac{N!}{N_p! N_q!}$$

and the minimum number of microstates would be 1, in the case where no mixing has occurred whatsoever. We can compute the change in entropy of this system, going from unmixed to completely mixed, using the Boltzmann equation:

$$\begin{aligned} \Delta S_{mix} &= k_B \left( \ln W_f - \ln W_i \right) \\ &= k_B \ln \left( \frac{N!}{N_p! N_q!} \right) \\ &= k_B \left( N \ln N - N - (N_p \ln N_p - N_p) - (N_q \ln N_q - N_q) \right) \\ &= k_B \left( (N_p + N_q) \ln N - N_p \ln N_p - N_q \ln N_q \right) \\ &= k_B \left[ N_p \ln \left( \frac{N}{N_p} \right) + N_q \ln \left( \frac{N}{N_q} \right) \right] \\ &= -k_B(N) \left[ \frac{N_p}{N} \ln \left( \frac{N_p}{N} \right) + \frac{N_q}{N} \ln \left( \frac{N_q}{N} \right) \right] \\ &= -k_B N (x_p \ln x_p + x_q \ln x_q) \end{aligned} \tag{5.1.1}$$

Which gives us an expression for the entropy of mixing in terms of the mole fraction of each species. Notice that both  $x_p$  and  $x_q$  are less than one, since they're mole fractions, and so  $\Delta S_{mix} > 0$  as expected. What's reassuring is that we could have derived an equivalent expression from a macroscopic description of the system instead of a microscopic one:

$$\begin{aligned} \Delta G_{mix} &= G_{mixed} - G_{unmixed} \\ &= (n_p \mu_p + n_q \mu_q)_{mixed} - (n_p \mu_p + n_q \mu_q)_{unmixed} \\ &= n_p (\mu_p^* + RT \ln x_p) + n_q (\mu_q^* + RT \ln x_q) - (n_p \mu_p^* + n_q \mu_q^*) \\ &= n_p RT \ln x_p + n_q RT \ln x_q \\ &= nRT \left( \frac{n_p}{n} \ln x_p + \frac{n_q}{n} \ln x_q \right) \\ &= nRT (x_p \ln x_p + x_q \ln x_q) \end{aligned} \tag{5.1.2}$$

At this point, recall from Equation (2.4.4) that  $S = -(\partial G / \partial T)_P$  which recovers the desired expression for the entropy in Equation (5.1.1). In the second line of the derivation above we made use of the definition of Gibbs free energy in terms of the chemical potential, Equation (4.1.7), and in the third line we utilized the reference state definitions defined in this section, in particular Equation (5.0.1). Lastly, notice that our expressions for  $\Delta G_{mix}$  and  $\Delta S_{mix}$  imply that  $\Delta H_{mix} = 0$ . Does this result make any sense?

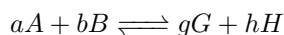
Yes! When mixing there is no bond breaking or forming going on. Hence, there is no enthalpy change going on.

## 5.2 The Thermodynamics of a Chemical Reaction

In the analysis of mixtures above, we treated all components in the system as unreactive and although unreactive mixtures can exhibit interesting behaviors such as phase transitions, the complexity of a thermodynamic system cannot be described without chemical reactions.

Recall from our study of phase transitions that we could compute the free energy of a phase transition from the chemical potentials as  $G = n^\alpha \mu^\alpha + n^\beta \mu^\beta$ . Significantly, this equation implies that *the transition will proceed to completion*. That is, if we suppose  $\mu^\beta < \mu^\alpha$  at a particular set of conditions, zero moles of phase  $\alpha$  will exist at equilibrium because that would be the state which minimizes the free energy of the system. From the perspective of mixing, the reason why phase transitions proceed to completion is because it involves no unmixing. In contrast, the progression of a chemical reaction is associated with the breaking down and building up of different reactants and products, respectively. So, a reaction which proceeds to completion is associated with *complete unmixing*, which is clearly entropically unfavorable. Hopefully this point provides some intuition behind why we study equilibrium in the first place. The distribution of products and reactants for a chemical reaction in equilibrium gives us vital information about the thermodynamic favorabilities of each species and, as we'll see later, are crucial for calculating some of these thermodynamic quantities<sup>2</sup>.

To begin our discussion on chemical reactions let's first establish some notation:



Here,  $A$ ,  $B$ ,  $G$ , and  $H$  are chemical species with respective reaction numbers  $a$ ,  $b$ ,  $g$ , and  $h$ . Additionally we'll define *reaction coefficients*  $\nu_A$ ,  $\nu_B$ ,  $\nu_G$ , and  $\nu_H$  as the reaction numbers for products and the opposite of the reaction numbers for the reactants. So, for a reaction like  $2\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O}$ ,

$$\nu_{\text{H}_2\text{O}} = 2, \quad \nu_{\text{H}_2} = -2, \quad \nu_{\text{O}_2} = -1$$

This formalism allows us to describe a chemical reaction similar to a mathematical equation, using the reaction coefficients such that

$$\sum_{i=1}^n \nu_i I_i = 0$$

where we sum over all species  $I_i$  in a reaction composed of  $n$  components.

Using the defined notation we'll approach defining a reaction energy in two ways. Firstly, we'll consider the difference between the chemical potentials of the products and reactants to deduce the free energy of reaction and secondly, we'll evaluate the differential free energy change with respect to the moles of reaction.

### 5.2.1 Free Energy of Reaction from Finite Differences

Here we'll consider a very direct approach of determining the free energy of a reaction, by representing it as the difference between the free energy of the products and of the reactants. Each of these moles of reaction are connected by the total number of moles involved in the reaction such that

$$\eta_i = \nu_i \eta_{rxn} \tag{5.2.1}$$

---

<sup>2</sup>Here I'll also mention the *Curtin-Hammett principle*, which concerns the distribution of products for a reaction as well, a more particular set of conditions. I mention this principle mainly caused I learned about it recently and still don't completely understand.

where  $\nu_i$  is the reaction coefficient, defined above. This allows us to define the change in Gibbs free energy of reaction as

$$\begin{aligned}\Delta G_{rxn} &= \eta_{react} \tilde{G}_{react} + \eta_{prod} \tilde{G}_{prod} \\ &= \nu_A \eta_{rxn} \tilde{G}_A + \nu_B \eta_{rxn} \tilde{G}_B + \nu_G \eta_{rxn} \tilde{G}_G + \nu_H \eta_{rxn} \tilde{G}_H \\ &= \eta_{rxn} (\nu_A \mu_A + \nu_B \mu_B + \nu_G \mu_G + \nu_H \mu_H)\end{aligned}\quad (5.2.2)$$

and dividing both sides by the total number of moles involved in the reaction affords

$$\Delta \tilde{G}_{rxn} = \nu_A \mu_A + \nu_B \mu_B + \nu_G \mu_G + \nu_H \mu_H \quad (5.2.3)$$

Let's stop for a moment and consider the result above. Since an initially prepared chemical system will continue reacting spontaneously until reaching equilibrium we can deduce that  $\Delta \tilde{G}_{rxn}$  is the amount of molar free energy evolved in this process. Naturally, this free energy change will depend on concentrations; if a system starts near equilibrium not much free energy will be evolved whereas if it starts far away from equilibrium there will be a much more significant free energy change. Let's try and determine this dependence on concentration.

Recall from Equation (5.0.2) that we can express the chemical potentials of each species in terms of reference potentials and the concentration of the respective species. Hence, we can rewrite Equation (5.2.3) as

$$\begin{aligned}\Delta \tilde{G}_{rxn} &= \nu_A (\mu_A^\circ + RT \ln[A]) + \nu_B (\mu_B^\circ + RT \ln[B]) \\ &\quad + \nu_G (\mu_G^\circ + RT \ln[G]) + \nu_H (\mu_H^\circ + RT \ln[H]) \\ &= \nu_A \mu_A^\circ + \nu_B \mu_B^\circ + \nu_G \mu_G^\circ + \nu_H \mu_H^\circ + RT \ln ([A]^{\nu_A} [B]^{\nu_B} [G]^{\nu_G} [H]^{\nu_H})\end{aligned}\quad (5.2.4)$$

where the right-side terms are representative of the standard state and are *independent of initial concentrations* whereas the left-side terms within the logarithm are *entirely dependent on concentrations*. Notice that if we choose to evaluate  $\Delta \tilde{G}_{rxn}$  at the standard state so that  $\Delta \tilde{G}_{rxn} = \Delta \tilde{G}_{rxn}^\circ$  then by definition the right-most term of Equation (5.2.4) must be zero.

In other words, the left-side terms of the equation express the amount of free energy released in a reaction if the reaction commenced at standard state and the right-side terms correct for the energy release in the event that species do not start at their standard state concentrations.

Unless this is the first chemistry class you've ever taken, you'll have seen the equation above already just with some different variable names. Suppose we define

$$\Delta \tilde{G}_{rxn}^\circ = \nu_A \mu_A^\circ + \nu_B \mu_B^\circ + \nu_G \mu_G^\circ + \nu_H \mu_H^\circ$$

as the *amount of free energy released in a chemical reaction that is initially prepared at its standard state* and

$$Q = [A]^{\nu_A} [B]^{\nu_B} [G]^{\nu_G} [H]^{\nu_H} = \frac{[G]^g [H]^h}{[A]^a [B]^b}$$

as the *reaction quotient*. Then, we're left with

$$\Delta \tilde{G}_{rxn} = \Delta \tilde{G}_{rxn}^\circ + RT \ln Q \quad (5.2.5)$$

as the *amount of free energy released in a chemical reaction that is prepared at some arbitrary conditions and allowed to reach equilibrium*.

The two unique terms in Equation (5.2.5) play very different roles in reaction thermodynamics and therefore warrant additional discussion. The first term imparts a *uniqueness* to the reaction and determines the specificity and cooperativity. Suppose we are developing a drug that must maintain a high affinity for a molecular target. Then, it is  $\Delta \tilde{G}_{rxn}^\circ$  which must be optimized. Although the second term affects the standard

Gibbs free energy change in response to product and reactant concentrations it does so in a *predetermined way*. That is, once initial conditions are determined than  $Q$  is fixed. Now that we have an intuitive understanding of this equation we'll consider the how it might change at equilibrium conditions.

As mentioned previously, we know that a chemical reaction will proceed to equilibrium at which point no more energy will be released and there is no more work the system can do on its surroundings<sup>3</sup>. In this case,  $\Delta\tilde{G}_{rxn} = 0$  and so we can rewrite Equation (5.2.5) as

$$\Delta\tilde{G}_{rxn}^{\circ} = -RT \ln K_{eq} \quad (5.2.6)$$

where

$$K_{eq} = \frac{[G]_{eq}^g [H]_{eq}^h}{[A]_{eq}^a [B]_{eq}^b} \quad (5.2.7)$$

is the *equilibrium constant* which denotes the relationship between reactant and product concentrations once the equilibrium state is reached.

Here's a example problem illustrating the utility of some of the equations we derived: The acid dissociation constant, denoted  $K_a$ , is a measure of the distribution of free protons and conjugate base in solution for some acid. Recall that the  $pK_a$  of a molecule is an important measure of its acidity and is useful in comparing the acidities of different organic compounds. The  $pK_a$  of acetic acid is 4.76. Calculate the free energy change when 1 M acetic acid, initially placed in neutral water with 1 mM acetate, reaches equilibrium.

Equation (5.2.5) will be of great use to us here. First, we can compute the standard molar Gibbs free energy change of reaction using Equation (5.2.6):

$$\Delta\tilde{G}_{rxn}^{\circ} = -RT \ln K_a = -(8.3145)(298) \ln(10^{-4.76}) = 27.16 \text{ kJ/mol}$$

Before we can compute the molar Gibbs free energy change of reaction we need the reaction quotient,  $Q$ . Luckily we're given everything we need to compute that as well,

$$Q = \frac{[H^+][A^-]}{[HA]} = \frac{(10^{-7})(10^{-3})}{1} = 10^{-10}$$

and we can compute the molar Gibbs free energy change as,

$$\Delta\tilde{G}_{rxn} = \Delta\tilde{G}_{rxn}^{\circ} + RT \ln Q = 27.16 + (8.3145)(298) \ln 10^{-10} = -29.89 \text{ kJ.mol}$$

which is our final answer.

## 5.2.2 The van't Hoff Equation

Recall from Equation (??) that, by definition, we can express the Gibbs free energy as  $\Delta G = \Delta H - T\Delta S$  so that Equation (5.2.6) can be rewritten to afford

$$\begin{aligned} \Delta\tilde{H}_{rxn}^{\circ} - T\Delta\tilde{S}_{rxn}^{\circ} &= -RT \ln K_{eq} \\ \ln K_{eq} &= \frac{-\Delta\tilde{H}_{rxn}^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta\tilde{S}_{rxn}^{\circ}}{R} \end{aligned} \quad (5.2.8)$$

Equation (5.2.8) is known as the *van't Hoff equation* and has exceptional utility because it allows us to disentangle the enthalpic and entropic contributions of the free energy by measuring the temperature dependence of the equilibrium constant. There are a few key takeaways from this equation that are worth noting:

1. At very high temperatures, the *entropic* contribution dominates and at very low temperatures, the *enthalpic* contribution dominates.

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<sup>3</sup>Recall that one definition of free energy is that it is the amount of work available the system has to do work on its surroundings.



2. If a reaction has a large *enthalpic* contribution, we would expect it to have a high temperature-dependence.
3. For exothermic reactions, increasing the temperature will shift the equilibrium *toward the reactants* since the right-hand side of the equation will become less positive and therefore  $\ln K_{eq}$  will become less positive implying  $K_{eq}$  has shrunk. This is the basis for le Châtelier’s principle.

As we know from, well... life... physical processes don’t typically proceed at discrete time increments. That is, using a chemical transformation as an example, the species involved in a reaction are continuously being transformed instead of reactants being spontaneously converted into products, waiting a sec, and then being spontaneously converted again. Thus, the “finite differences” approach we took to determining the Gibbs free energy change of reaction above may be an alarm for some concern. Although  $Q$  allows us to compute  $\Delta\tilde{G}_{rxn}^\circ$  at any set of reactant and product concentrations, Equation (5.2.5) is evaluated for a *fixed* set of these conditions. However, we know from physical intuition that as a reaction proceeds, reactants will be converted to products and therefore the concentrations of each species will be constantly changing. So what is the usefulness of Equation (5.2.5)? If you’re a biochemist, fear not, since the “chemostatic” approach is actually quite common in cells because reactant and product concentrations are controlled by a network of biochemical reactions.

However, if you’re like me and don’t care for cells, this reassurance is anything but reassuring. In the next section we’ll consider an approach which accounts for these differential changes in reactant and product concentrations.

### 5.2.3 Free Energy of Reaction from Differentials

In contrast to the method of finite differences, now we will consider a differential change in the chemical potentials which results in a more mathematical yet hopefully less conceptually-exhausting method of deriving the free energy change for a reaction. Recall Equation (4.1.12) that we can express the differential change in molar Gibbs free energy as a sum of chemical potentials,

$$d\tilde{G} = \sum_{i=1}^n \mu_i$$

and using the reaction defined above in Section 5.2.1 we can express a differential change in Gibbs free energy as

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_G dn_G + \mu_H dn_H \quad (5.2.9)$$

An advantage we gain when studying the free energy of reaction from a differential approach is that we can concern ourselves with the total amount of reactant and product present (defined earlier as  $\eta_i$  for each species  $i$ ) as opposed to the total amount of species *involved* in the reaction (defined earlier as  $\eta_{rxn}$ ) which was necessary when handling the free energy of reaction from the perspective of finite differences. Hence, we can define the *extent of reaction*<sup>4</sup>, denoted  $\xi$ , to describe how the number of moles of each species involved in a reaction changes as the reaction progresses. Intuitively, value of  $\xi$  represents how much the reactant has converted to product<sup>5</sup>.

Because the variations of reaction we’ll consider are infinitesimal, thereby leaving the chemical potential of each species effectively unchanged, we can express a differential change in moles for each species as

$$dn_i = \nu_i d\xi$$

where  $\nu_i$  is the reaction coefficient as defined earlier. Substituting this result into Equation (5.2.9) affords an expression for a differential change in Gibbs free energy:

$$dG = \mu_A \nu_A d\xi + \mu_B \nu_B d\xi + \mu_G \nu_G d\xi + \mu_H \nu_H d\xi$$

<sup>4</sup> $\xi$  can sometimes also be referred to as the “reaction coordinate.”

<sup>5</sup>Relating this back to the finite differences approach, since we did not take into account any changes in reactant and product concentrations we could think of our method in Section ?? as taking place at a fixed value of  $\xi$ .

Notice that we can rewrite this expression as the differential equation

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \mu_A \nu_A + \mu_B \nu_B + \mu_G \nu_G + \mu_H \nu_H = \Delta \tilde{G}_{rxn} \quad (5.2.10)$$

where the equality with  $\Delta \tilde{G}_{rxn}$  comes by definition (and also Equation (5.2.3)). Notice that we define the partial derivative at a constant temperature and pressure because otherwise the chemical potentials of each species would be changing. In this instance, we don't want that.

The significance of Equation (5.2.10) is clear once we recall that the Gibbs free energy acts as an indicator of spontaneity at a constant temperature and pressure. If we observe  $G$  increasing as  $\xi$  increases (i.e.,  $(\partial G/\partial \xi)_{T,P} > 0$ ) then we'd expect the reaction to proceed in the direction that converts products back into reactants, that is, we'd expect  $\xi$  to decrease. Thus, when plotted against the extent of a reaction, the total Gibbs free energy serves as a reaction potential.

To illustrate some of these key principles, let's consider a simple chemical reaction  $A \rightleftharpoons B$  with  $\mu_A^\circ$  and  $\mu_B^\circ$  as the standard chemical potentials for  $A$  and  $B$ , respectively. Additionally, assume that there are  $n_A$  moles of  $A$  and  $n_B$  moles of  $B$  such that  $n_A + n_B = n$  where  $n$  is the total number of moles present. Then, the number of moles of reactant and product ( $n_A$  and  $n_B$ , respectively) can be expressed as  $n_A = n(1 - \xi)$  and  $n_B = n\xi$  where the initial solution is composed of entirely species  $A$ . Lastly, suppose that the molar volume of  $A$  is  $\tilde{V}_A$  and that of  $B$  is  $\tilde{V}_B$  and for the sake of simplicity assume that  $\tilde{V}_A = \tilde{V}_B = V$ . By Equations (4.1.12) and (5.0.2) we can express the Gibbs free energy with our new notation as

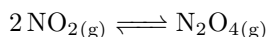
$$\begin{aligned} G &= \sum_{i=1}^{\# \text{ species}} \mu_i n_i = \mu_A n_A + \mu_B n_B \\ &= (\mu_A^\circ + RT \ln[A])n_A + (\mu_B^\circ + RT \ln[B])n_B \\ &= n(1 - \xi) \left[ \mu_A^\circ + RT \ln \left( \frac{n(1 - \xi)}{V} \right) \right] + n\xi \left[ \mu_B^\circ + RT \ln \left( \frac{n\xi}{V} \right) \right] \end{aligned}$$

Recall from Equation (5.2.10) that we can compute the change in molar Gibbs free energy of reaction as the partial derivative of  $G$  with respect to  $\xi$ . Moreover, suppose we "standardize" the reaction and let  $n_A + n_B = n = 1$ . Thus,

$$\begin{aligned} \Delta \tilde{G}_{rxn} &= \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \frac{\partial}{\partial \xi} \left\{ (1 - \xi) \left[ \mu_A^\circ + RT \ln \left( \frac{1 - \xi}{V} \right) \right] + \xi \left[ \mu_B^\circ + RT \ln \left( \frac{\xi}{V} \right) \right] \right\} \\ &= -\mu_A^\circ - RT \left[ 1 + \ln \left( \frac{1 - \xi}{V} \right) \right] + \mu_B^\circ + RT \left[ 1 + \ln \left( \frac{\xi}{V} \right) \right] \\ &= \mu_B^\circ - \mu_A^\circ + RT \left[ -1 - \ln \left( \frac{1 - \xi}{V} \right) + 1 + \ln \left( \frac{\xi}{V} \right) \right] \\ &= \mu_B^\circ - \mu_A^\circ + RT \ln \left( \frac{\xi}{1 - \xi} \right) \\ &= \Delta \tilde{G}_{rxn}^\circ + RT \ln \left( \frac{\xi}{1 - \xi} \right) \quad (5.2.11) \end{aligned}$$

Hopefully it's clear how this equation is the same as Equation (5.2.5). If not, I'll try to make it so. Recall that we defined  $n_A = n(1 - \xi)$  and  $n_B = \xi$  so that the expression in the logarithm becomes  $n_B/n_A$ . These are concentrations though! Nice catch! Recall that we let  $\tilde{V}_A = \tilde{V}_B = V$  so that the volumes cancel out in the expression, hence why we're left with moles instead of concentrations.

The whole  $\xi$  thing get's pretty weird I'd say, so here's an example problem illustrating how we might use it to analyze a system: Assume that a sealed vessel at a constant pressure of 1 bar initially contains 2 moles of  $\text{NO}_{2(g)}$ . The system is allowed to equilibrate with respect to the reaction



The number of moles of  $\text{NO}_{2(g)}$  and  $\text{N}_2\text{O}_{4(g)}$  at equilibrium are  $2 - 2\xi$  and  $\xi$ , respectively, where  $\xi$  is the extent of reaction. Derive an expression for the entropy of mixing as a function of  $\xi$ .

Okay! We'll start from the change in Gibbs free energy of mixing:

$$\begin{aligned}\Delta G_{mix} &= G_{\text{mixed}} - G_{\text{unmixed}} \\ &= (n_1\mu_1)_{\text{mixed}} - (n_2\mu_2)_{\text{unmixed}}\end{aligned}$$

where  $n_1$  and  $n_2$  represent the number of moles of  $\text{NO}_{2(g)}$  and  $\text{N}_2\text{O}_{4(g)}$ , respectively, and  $\mu_1$  and  $\mu_2$  represent their respective chemical potentials. Continuing, and using Equation (5.0.1) to substitute for the chemical potentials which aren't in their standard state in the equation above, we have

$$(n_1\mu_1)_{\text{mixed}} - (n_2\mu_2)_{\text{unmixed}} = n_1(\mu_1^* + RT \ln x_1) + n_2(\mu_2^* + RT \ln x_2) - (n_1\mu_1^* + n_2\mu_2^*)$$

where  $x_1$  and  $x_2$  represent the respective mole fractions of  $\text{NO}_{2(g)}$  and  $\text{N}_2\text{O}_{4(g)}$ . Hence,

$$\begin{aligned}\Delta G_{mix} &= n_1(\mu_1^* + RT \ln x_1) + n_2(\mu_2^* + RT \ln x_2) - (n_1\mu_1^* + n_2\mu_2^*) \\ &= n_1RT \ln x_1 + n_2RT \ln x_2 \\ &= (n_1 + n_2)RT \left[ \left( \frac{n_1}{n_1 + n_2} \right) \ln x_1 + \left( \frac{n_2}{n_1 + n_2} \right) \ln x_2 \right] \\ &= nRT(x_1 \ln x_1 + x_2 \ln x_2)\end{aligned}$$

where  $n$  represents the total number of moles in solution. You may recognize this expression from Equation (5.1.2). That's because they're the same thing. Noting that the enthalpy change associated with mixing is zero, we can determine the entropy change by the relationship  $\Delta G = -T\Delta S$  to afford the entropy as a function of mole fractions:

$$\Delta S_{mix} = -nR(x_1 \ln x_1 + x_2 \ln x_2)$$

Now to express the mole fractions of each species as a function of  $\xi$ . Notice that the vessel initially contains 2 moles of reactant so that when  $\xi = 0$ , the number of moles is 2. As  $\xi$  increases, the moles of reactant will decrease by  $2\xi$  (according to the reaction coefficient) and the moles of product will increase by  $\xi$  (again, according to the reaction coefficient). Hence, the mole fractions can be expressed as

$$x_1 = \frac{2 - 2\xi}{2 - \xi}, \quad \& \quad x_2 = \frac{\xi}{2 - \xi}$$

which affords an expression for the entropy of mixing in terms of the extent of reaction:

$$\Delta S_{\text{mix}} = -nR \left[ \frac{2 - 2\xi}{2 - \xi} \ln \left( \frac{2 - 2\xi}{2 - \xi} \right) + \frac{\xi}{2 - \xi} \ln \left( \frac{\xi}{2 - \xi} \right) \right]$$

## 5.3 Conformational Equilibrium

In this section we'll apply everything we've learned about the thermodynamics of equilibrium and apply it to the conformational change of a protein. Surprisingly, a useful model for conformational equilibrium is a *two-state system* where a protein exists in either a folded (native) or unfolded state. While this seems like an over-simplified model, we're already familiar with plenty of physical processes which exhibit this behavior: The conformational equilibrium between the two chair conformers of cyclohexane and the keto-enol tautomerization of a hydrocarbon are two great examples.

When dealing with conformational changes there are a few common aspects among every reaction of this type: They are reversible reactions, no atoms are (net) added or removed from the molecule, and no covalent

bonds are “broken,” only rearranged.

The conformational change we’ll consider now is the unfolded and folded conformers of a protein in equilibrium with one another, modeled by  $U \rightleftharpoons N$  where  $U$  and  $N$  represent the unfolded and native forms of the protein, respectively. This transformation has an equilibrium constant afforded by

$$K_{eq} = \frac{[N]}{[U]} \quad (5.3.1)$$

Already the beauty of this model is becoming clear: By knowing only the relative concentrations of the native and unfolded states we can determine some thermodynamic quantities that describe the system, namely,  $K_{eq}$  and  $\Delta\tilde{G}^\circ$ .

In practice, determining the concentrations of the native and unfolded states of the protein can be quite complex. One method has proven useful for studying proteins in conformational equilibrium is *circular dichroism spectroscopy*<sup>6</sup>, or just CD spectroscopy. Circular dichroism relies on the difference in the absorption of left and right circularly polarized light, typically in the range of 200-230 nm. At these wavelengths, both  $\alpha$ -helices and  $\beta$ -sheets display strong negative “ellipticity”<sup>7</sup> due to the regular and repetitive geometry of the structures. In contrast, unfolded coils consist of primarily random coils and don’t display any sort of particular ellipticity. Hence, the CD spectra of folded and unfolded proteins will look very different.

Unsurprisingly, the experimental spectrum will be a *superposition* of the basis spectra, that is, the experimental spectrum will be a linear combination of the spectra for the unfolded and native proteins. The presence of an *isosbestic point* on the spectra supports this theory. Below is a CD spectra.

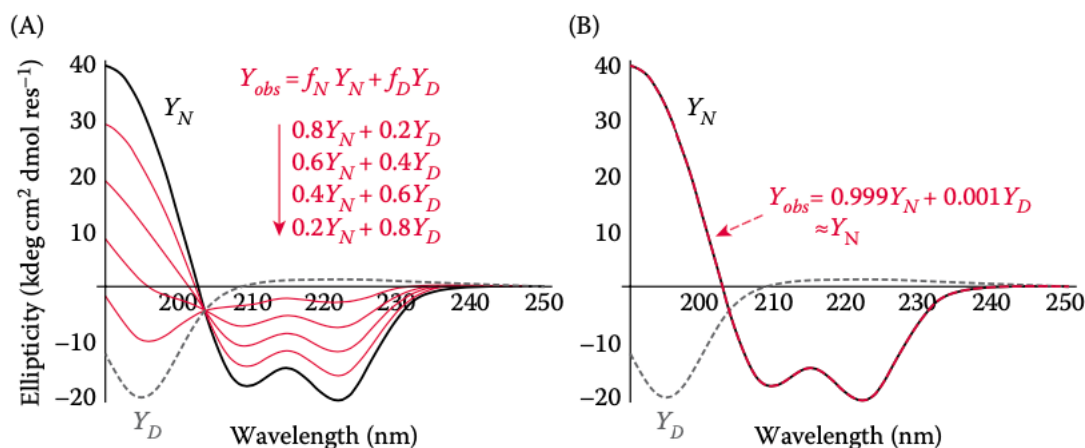


Figure 5.1: Circular dichroism spectrum, illustrating superposition of basis spectra. The *isosbestic point* is the point at which all curves intersect. (A) Spectra of mixtures from the measurable equilibrium range. (B) Spectrum for a mostly folded mixture.

Now we will introduce the simplest, both experimentally and conceptually, model for conformational change, the *thermal unfolding transition*. Below is a theoretical graphic illustrating the distribution of conformers for the two-state system during thermal unfolding. Note that Dr. Barrick uses  $Y_D$  to denote the protein in a “denatured” state. I’ve been using  $Y_U$  to denote the same quantity.

Above, we see that by increasing the temperature of a system we can shift the equilibrium constant for most proteins toward the unfolded state. In the “baseline” regions of the native and unfolded states of the protein, the observed signal  $Y_{obs}$  is insensitive to changes in temperature. However, when the equilibrium constant shifts to the measurable range, the spectroscopic signal changes sharply with changes in temperature. The center of

<sup>6</sup> “Circular” refers to the polarization of light being measured and “dichroism” refers to the two types of light we can measure using this method.

<sup>7</sup> Ellipticity is a measure of CD strength and is proportional to the amount of structured molecules present.

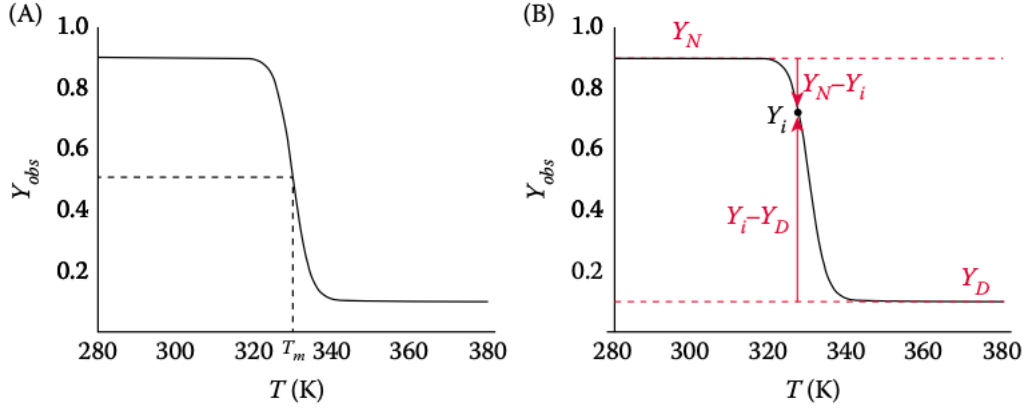


Figure 5.2: (A) The observed signal, the solid black line, shows a sharp transition between the native and denatured baselines. The value  $T_m$  is fixed at the arbitrarily fixed conditions in the graph. (B) The baselines play a key role in determining the value of fractional populations and equilibrium constants. The fractional populations  $f_N$  and  $f_U$  can be described geometrically with red arrows connecting the baseline to the observed signal.

this transition, where the sample is such that  $[N] = [U]$ , is referred to as the *midpoint temperature*, oftentimes denoted as  $T_m$ . Suppose that we could measure the observable  $Y_{obs}$ . Then how could we determine  $K_{eq}$  from a set of  $Y_{obs}$  values?

The key idea lies in Figure 5.1, where we see that the signal  $Y_{obs}$  is linearly proportional to the amount of each state present. If we let  $f_N$  and  $f_U$  represent the *fractional populations*<sup>8</sup> of the native and unfolded states, respectively, we can represent the observed signal  $Y_{obs}$  as

$$Y_{obs} = f_U Y_U + f_N Y_N \quad (5.3.2)$$

Since  $f_U + f_N = 1$  by the conservation of mass, we can rewrite the expression for  $Y_{obs}$  to afford

$$\begin{aligned} Y_{obs} &= f_N Y_N + (1 - f_N) Y_U \\ &= f_N Y_N + Y_U - f_N Y_U \\ &= f_N (Y_N - Y_U) + Y_U \\ f_N &= \frac{Y_{obs} - Y_U}{Y_N - Y_U} \end{aligned} \quad (5.3.3)$$

A similar expression can be derived for the fractional population of  $Y_U$ :

$$f_U = \frac{Y_N - Y_{obs}}{Y_N - Y_U} \quad (5.3.4)$$

With Equations (5.3.3) and (5.3.4) we can give a description of the equilibrium constant, after some algebraic manipulation. Start by noticing

$$\frac{f_N}{f_U} = \left( \frac{Y_{obs} - Y_U}{Y_N - Y_U} \right) \left( \frac{Y_N - Y_U}{Y_N - Y_{obs}} \right) = \frac{Y_{obs} - Y_U}{Y_N - Y_{obs}}$$

and that we could have also expressed the fractional populations as  $f_U = [U]/([U] + [N])$  and  $f_N = [N]/([U] +$

<sup>8</sup>The fractional populations  $f_U$  and  $f_N$ , which range from zero to 1, can be thought of as probabilities, as long as the sample is large enough for good averaging (by the law of large numbers).

$[N]$ ) so that the ratio above could be alternatively expressed as

$$\frac{f_N}{f_U} = \left( \frac{[N]}{[U] + [N]} \right) \left( \frac{[U] + [N]}{[U]} \right) = \frac{[N]}{[U]} = K_{eq} \quad (5.3.5)$$

Geometrically, we can think of  $K_{eq}$  as the ratio of the two red arrows in Figure 5.2. For this reason, we need enough sample points in the “baseline” regions to know where to start these arrows when trying to analyze CD spectroscopy data. With this in mind, we can think of the conformational transition as containing three distinct regions: The native conformer baseline, the transition region, and the unfolded conformer baseline.

Referring back to Equation (5.3.5), we have that

$$K_{eq} = \frac{Y_{obs} - Y_U}{Y_N - Y_{obs}} \quad (5.3.6)$$

which allows us to (finally) rewrite the observable quantity  $Y_{obs}$  as

$$Y_{obs} = \frac{Y_U + Y_N K_{eq}}{1 + K_{eq}} = \frac{Y_U + Y_N e^{-(\Delta\tilde{H}^\circ - T\Delta\tilde{S}^\circ)/RT}}{1 + e^{-(\Delta\tilde{H}^\circ - T\Delta\tilde{S}^\circ)/RT}} = \frac{Y_U + Y_N e^{-(\Delta\tilde{H}^\circ/RT)} e^{(\Delta\tilde{S}^\circ/R)}}{1 + e^{-(\Delta\tilde{H}^\circ/RT)} e^{(\Delta\tilde{S}^\circ/R)}} \quad (5.3.7)$$

Equation (5.3.7) illustrates the enthalpy and entropy dependence of the observable  $Y_{obs}$ . Moreover, we see that  $Y_{obs}$  varies with temperature. Naturally, the next question we might ask is whether or not  $\Delta\tilde{H}^\circ$  and  $\Delta\tilde{S}^\circ$  depend on temperature as well (the answer is that they do).

You may recall that we have numerous definitions and expressions for the heat capacity. In this instance, while we’re trying to determine the temperature dependence of the enthalpy and entropy, we’ll mainly be concerned with the relationship  $d\tilde{H} = \tilde{C}_P dT$ . Similarly, we have that  $d\tilde{S} = (\tilde{C}_P/T) dT$ . UNFINISHED

## CHAPTER

# 6

# CALORIMETRY AND THERMOCHEMISTRY

*Calorimetry*

- *Scientist*

As the name(s) imply, calorimetry and thermochemistry rest on the analysis of heat energy and exchange with a system's surroundings. As such, the enthalpy of reaction will be of primary consideration constantly, in (slight) contrast to the discussion on thermodynamics previously. This contrast poses a question: Why is it that the entropy of a reaction is emphasized so heavily in our formal development of thermodynamics, whereas when we begin to analyze chemical reactions and processes everything seems to be dominated by enthalpy?

The answer to this question lies in *how we define a system*. Oftentimes, the thermodynamic system of interest in calorimetry and thermochemistry is defined as the reacting molecules and is typically closed (the system is exchanging heat with the surroundings but not matter). In this system, the bonds of each molecule are broken and reformed to create a lower energy ensemble of particles. This results in the *enthalpy of reaction*.

When this heat is released (or absorbed) from a reaction it goes into heating up (or cooling down) the surroundings, by the second law of thermodynamics. If we alter our POV of the system from the collection of particles to the collection of particles *and* the surroundings, we can imagine that the system is isolated. Then, since the energy of an isolated system must be conserved, the latent energy<sup>1</sup> in the “energy-rich” bonds of the molecules that go into heating up the surroundings don't actually change the energy of the system.

The hotter surroundings will be associated with a greater entropy since

$$\Delta S_{surr} = \int_{T_{low}}^{T_{high}} \frac{C_{P,surr}(T)}{T} dT > 0$$

where the change in temperature of the surroundings can be determined by

$$-\Delta H_{rxn} = \int_{T_{low}}^{T_{high}} C_{P,surr}(T) dT$$

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<sup>1</sup>latent energy

Thus, if we consider the system as including both the reacting molecules and the immediate surroundings, we would say that reactions occur because they are *entropically favored*—there are not as many configurations associated with the energy “trapped” in bonds as compared to the energy liberated into thermal motion.

## 6.1 Calorimetry

Calorimetry is the process of measuring the amount of heat released or absorbed during a chemical reaction. There are numerous different types of calorimetry to consider: Constant-pressure, constant-volume, and differential scanning calorimetry are all tools which have proven their use in many fields of physical chemistry.

No matter the method by which heat exchange is measured, calorimetry is useful in the succeeding section on *thermochemistry*, the study of heat energy. As we’ll see, calorimetry provides a much more direct measurement of various equilibria, including conformational equilibria discussed previously.

### 6.1.1 Differential Scanning Calorimetry

*Differential scanning calorimetry* (DSC) is a technique in which the difference in amount of heat required to increase the temperature of a sample, i.e., the heat capacity, is measured as a function of temperature. This “differential” heat capacity is denoted  $\delta\tilde{C}_P$ . As the name implies, our goal is to make the differences in temperature at each step we measure the difference in heat as small as possible in order to accurately measure the heat capacity of a substance.

Since unfolded and folded proteins have different heat capacities, DSC is useful in elucidating the structures of different conformers for the protein. As we saw earlier in Section 5.3 on conformational equilibrium, the fastest rate of change between the native and unfolded state occurs at  $T_m$ , the midpoint temperature. This is where the spike occurs in Figure 6.1A.

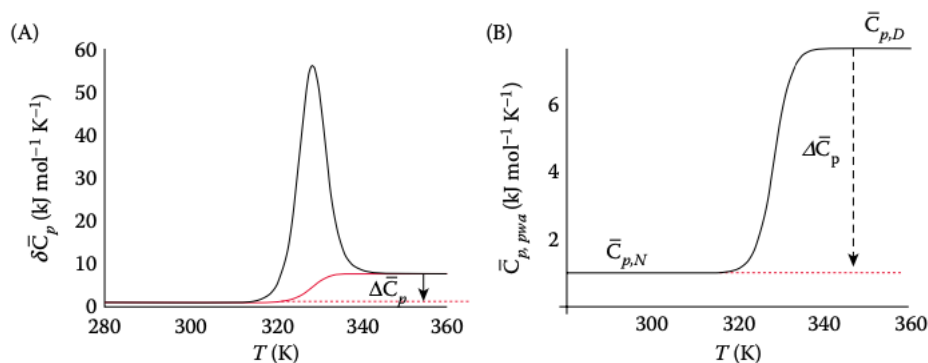


Figure 6.1: (A) A DSC folding transition (black line) superimposed on the population-weighted average heat capacity (red line denoted by  $\tilde{C}_{P,pwa}$ , shown in (B) as black line). The area between the black and red lines is the enthalpy of unfolding for the reaction. (B) An expanded view of the population-weighted average heat capacity. Note that the difference between the two baselines is the change in molar heat capacity.

Wait a minute... does the sharp peak we see at  $T_m$  even make sense? An increase in heat capacity certainly makes sense; after all, the heat capacity of the unfolded state is greater than that of the native state. However, if that were the only explanation, we’d expect a step function rather than a peak.

To rationalize this result we’ll have to do some math. We can express the measured differential heat capacity as

$$\delta\tilde{C}_P = \tilde{C}_{P,pwa} + \tilde{C}_{P,ex} \quad (6.1.1)$$

where  $\tilde{C}_{P,pwa}$  represents the population-weighted average heat capacity of the sample<sup>2</sup>, and  $\tilde{C}_{P,ex}$  represents

<sup>2</sup>The “population-weighted average” can be thought of as the sum of the heat capacities of native and unfolded proteins multiplied by their respective fractional populations. I’m trying to find a way to rephrase the term “weighted average” but I feel



the “excess” heat capacity which must be added to  $\tilde{C}_{P,pwa}$  to afford the measured  $\delta\tilde{C}_P$ . We can rewrite  $\tilde{C}_{P,pwa}$  in terms of the heat capacities for the native and unfolded states to afford a new expression for  $\delta\tilde{C}_P$ :

$$\begin{aligned}\delta\tilde{C}_P &= f_N\tilde{C}_{P,N} + f_U\tilde{C}_{P,U} + \tilde{C}_{P,ex} \\ &= f_N\tilde{C}_{P,N} + (1 - f_N)\tilde{C}_{P,U} + \tilde{C}_{P,ex} \\ &= \tilde{C}_{P,U} + f_N\Delta\tilde{C}_{P,N} + \tilde{C}_{P,ex}\end{aligned}\tag{6.1.2}$$

To secure a better understanding of the shape of the DSC curve we need an analytical expression for  $\tilde{C}_{P,ex}$ . This can be determined from analyzing the differential enthalpy,  $\delta H$ . Unlike the heat capacity,  $dH$  is simply a linear combination of the weighted averages for the native and unfolded state since enthalpy is a state function:

$$\begin{aligned}\delta\tilde{H} &= f_N\tilde{H}_N + f_U\tilde{H}_U \\ &= \tilde{H}_U + f_N\Delta\tilde{H}\end{aligned}\tag{6.1.3}$$

Equation (6.1.3) can be obtained by following a similar algebraic approach as was taken to afford Equation (6.1.2). Because DSC measures heat capacity, we must find a way to relate these enthalpies to the heat capacity of a protein. Lucky for us the heat capacity at a constant pressure is equal to the partial derivative of the enthalpy with respect to temperature:

$$\begin{aligned}\delta\tilde{C}_P &= \left(\frac{\partial\delta\tilde{H}}{\partial T}\right)_P \\ &= \left(\frac{\partial(\tilde{H}_U + f_N\Delta\tilde{H})}{\partial T}\right)_P \\ &= \left(\frac{\partial\tilde{H}_U}{\partial T}\right)_P + f_N\left(\frac{\partial\Delta\tilde{H}}{\partial T}\right)_P + \Delta\tilde{H}\left(\frac{\partial f_N}{\partial T}\right)_P\end{aligned}\tag{6.1.4}$$

The first two derivatives are simply expressions for heat capacity which sum to afford  $\tilde{C}_{P,pwa}$  by Equation (6.1.2). Therefore, we are left with

$$\tilde{C}_{P,ex} = \Delta\tilde{H}\left(\frac{\partial f_N}{\partial T}\right)_P\tag{6.1.5}$$

which explains where the “extra” heat capacity comes from.

How can we interpret Equation (6.1.5)? Firstly, it should be clear that the large amplitude of the peak comes from the derivative term, since the derivative of the transition is so large. At the baseline values, where there is no change in the fractional populations of the native and unfolded states, the derivative term goes to zero and we see the plots in Figure 6.1A superimposed on one another.

Alternatively we could relate this unexpected behavior to what we already know about phase transitions: Just as how in a phase transitions all energy being put into the system goes into breaking interactions rather than raising the temperature, in protein folding the energy being put into the system goes into altering the conformation of the protein rather than raising the temperature of the system.

Our goal now is to fit DSC folding transitions. To do this, we’ll start by expressing the derivative in Equation (6.1.5) in terms of some protein folding parameters. Note that

$$\begin{aligned}f_N &= K_{eq}f_U \\ &= K_{eq}(1 - f_N) \\ &= K_{eq} - f_NK_{eq} \\ f_N(1 + K_{eq}) &= K_{eq} \\ f_N &= \frac{K_{eq}}{K_{eq} + 1}\end{aligned}$$

---

the name itself is already pretty self-explanatory.

and so we can compute the derivative as

$$\begin{aligned}\left(\frac{\partial f_N}{\partial T}\right)_P &= \frac{\partial}{\partial T} \left( \frac{K_{eq}}{K_{eq} + 1} \right)_P \\ &= \frac{(K_{eq} + 1) - K_{eq}}{(K_{eq} + 1)^2} \frac{\partial K_{eq}}{\partial T} \\ &= \frac{1}{(K_{eq} + 1)^2} \frac{\partial K_{eq}}{\partial T}\end{aligned}\quad (6.1.6)$$

At this point both Dr. Barrick and Dr. Fried make a substitution that I don't think either of them ever explain once which, understandably, is confusing. So, let me make it more clear. Notice that

$$\frac{\partial \ln K_{eq}}{\partial T} = \frac{1}{K_{eq}} \frac{\partial K_{eq}}{\partial T} \Rightarrow K_{eq} \frac{\partial \ln K_{eq}}{\partial T} = \frac{\partial K_{eq}}{\partial T}$$

Thus, we can rewrite Equation (6.1.6) as

$$\left(\frac{\partial f_N}{\partial T}\right)_P = \frac{1}{(K_{eq} + 1)^2} \frac{\partial K_{eq}}{\partial T} = \frac{K_{eq}}{(K_{eq} + 1)^2} \frac{\partial \ln K_{eq}}{\partial T} \quad (6.1.7)$$

Why even bother making our lives more difficult in this way? Recall Equation (5.2.8), namely, the van't Hoff equation, which relates the natural logarithm of the equilibrium constant to relevant thermodynamic quantities. Taking the derivative of the van't Hoff equation with respect to temperature affords

$$\left(\frac{\partial f_N}{\partial T}\right)_P = \frac{K_{eq}}{(K_{eq} + 1)^2} \frac{\Delta \tilde{H}}{RT^2}$$

The left-most term of the right hand side in the equation above is known as the “spread over states” term, alternatively expressed as

$$\frac{K_{eq}}{(K_{eq} + 1)^2} = \frac{K_{eq}}{K_{eq} + 1} \times \frac{1}{K_{eq} + 1} = f_N f_U \quad (6.1.8)$$

In addition to the fact that this expression *peaks at*  $T_m$ , the spread over states term appears in a variety of conformational equilibria such as ligand-binding interactions. For two-state systems, such as the one we're currently interested in, it represents the extent to which the population is spread out over  $N$  and  $U$ .

Putting everything we have together finally, our expression to fit the DSC curve is given as

$$\delta \tilde{C}_P = \tilde{C}_{P,U} + f_N \Delta \tilde{C}_{P,N} + \frac{K_{eq}}{(K_{eq} + 1)^2} \frac{\Delta \tilde{H}^2}{RT^2} \quad (6.1.9)$$

### 6.1.2 Bomb Calorimetry (Constant Volume Calorimetry)

To measure the heat associated with a chemical transformation (most commonly combustion) we can use bomb calorimetry. In a bomb calorimetry experiment, we ignite a (typically highly exothermic) chemical reaction in a container of a fixed volume and record the change in temperature of the water reservoir surrounding the calorimeter. Because  $dV = 0$ , there is no work done by the system and by the first law of thermodynamics we have that  $q = \Delta U$ . This heat will go into warming up the vessel and water bath. If we define our thermodynamic system as being the reaction, vessel, and water bath, all of which are encased in a thick diathermal container,<sup>3</sup> no heat is lost to the surroundings.

The tricky part of this sort of experiment is determining the heat capacity of the calorimeter which will be some weighted average of the heat capacity of the steel vessel and the water:

$$C_{V,\text{calorimeter}} = n_{\text{water}} \tilde{C}_{V,\text{water}} + n_{\text{vessel}} \tilde{C}_{V,\text{vessel}}$$

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<sup>3</sup>This is a fancy way of saying no heat can be exchanged through the container.

In practice, we can evaluate the heat capacity of the calorimeter (often referred to as the *calorimeter constant*) by performing a reaction with a known  $\Delta U_{rxn}$  and working backwards:

$$\Delta U_{rxn} = \Delta T(n\tilde{C}_{V,water} + C_{cal})$$

As we've seen before, at a constant pressure  $q = \Delta H$  so that the calorimeter constant can be used to measure  $\Delta H_{rxn}$ :

$$\Delta H_{rxn} = C_{P,cal}\Delta T \quad (6.1.10)$$

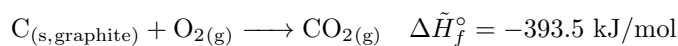
If we performed this reaction at 298 K and 1 atm we will have measured  $\Delta H_{rxn}^\circ$ , by definition.

## 6.2 Thermochemistry

Thermochemistry is the study of heat energy associated with chemical reactions and physical transformations. Chemical reactions may absorb or release heat, those being endothermic and exothermic reactions, respectively. In combination with entropic calculations, the spontaneity of a chemical reaction may be determined from the Gibbs free energy change.

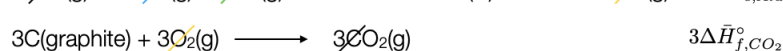
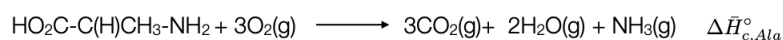
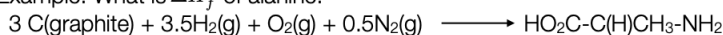
### 6.2.1 Heats of Formation

The *standard enthalpy of formation*, or just *standard heat of formation* is the change in enthalpy during the formation of 1 mole of a substance from its constituent elements with all substances in their standard states. An example reaction which satisfies these conditions might be the formation of carbon dioxide:



The true utility of heats of formation rest on the fact that enthalpy is a state function which permits the use of *Hess's law*, stating that the heat of any reaction is equal to the sum of the heats of reaction which in sum are equivalent to the overall reaction. Here is an entire example I've stolen from the lecture slides because (i) it's a good example of using Hess's law and (ii) as if I'm gonna type all that out for a concept that I already understand very well.

Example: What is  $\Delta \tilde{H}_f^\circ$  of alanine:



$$\Delta \tilde{H}_{f,Ala}^\circ = -\Delta \tilde{H}_{c,Ala}^\circ + 3 \Delta \tilde{H}_{f,CO_2}^\circ + 2 \Delta \tilde{H}_{f,H_2O}^\circ + \Delta \tilde{H}_{f,NH_3}^\circ$$

Figure 6.2: Using Hess's law to determine the heat of formation of the amino acid alanine.

As a consequence of our definition,  $\Delta H_f^\circ$  will be zero for pure elements in their most stable states. However, this is quite alright because “absolute enthalpy” is already something we've determined is arbitrary.

Entropy, however, is different. We can define *absolute molar entropies* for each substance by the third law of thermodynamics. Moreover, it is necessarily nonzero for all substances in their pure forms.

What would a discussion on thermodynamics be without the Gibbs free energy? Since  $\Delta G_f^\circ$  depends on the enthalpy of formation it is also not possible to define this quantity on an absolute scale. Hence, the common

convention is to define  $\Delta G_f^\circ$  to be zero for elements in their most stable states. In principle, this ignores the absolute entropy of an element, however, when computing  $\Delta G_{rxn}^\circ$ , this contribution goes away and we have nothing to fear. That is to say, we can define entropy on an absolute scale but it is not necessary to do so to determine  $\Delta S_{rxn}^\circ$ .

Here is an example illustrating the use of heats of formation and thermodynamic cycles: Suppose I'm interested in developing a catalyst to perform the following chemical reaction:

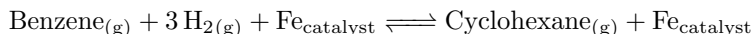


In a constant pressure calorimeter I combust benzene at STP and find that the temperature of 10 kg of water in the calorimeter increases by 6°C. My friend Sai runs the same experiment, this time using only 1 kg of water in his calorimeter, and finds that the temperature of the water reservoir increases by 58.5°C. Why was the temperature increase of Sai's experiment not simply ten times greater than that of my experiment?

Instead of doing math I'll offer a conceptual answer to this question. Obviously with less water in the calorimeter, the temperature of the water will increase by more because the specific heat capacity is the amount of heat required to raise the temperature of a kilogram of a substance by a unit celsius. Hence, with more mass and the same heat afforded to the system there will be a smaller change in temperature. However, note that the heat capacity is *not constant*, and *can vary significantly over large temperature ranges*. In Sai's experiment there was a large increase in temperature and so the heat capacity of the water increased enough to illustrate an experimental difference in the expected temperature change of the reservoir.

Ultimately, the discrepancy we see is due to the fact that the heat capacity of all substances is a function of the temperature, and in particular, increases with temperature.

With a year of committed research I've finally discovered a catalyst that can hydrogenate benzene, with the caveat that it works only at 400 K, where the following reaction takes place:



Our work isn't done, however, because now I am interested in determining the standard enthalpy of reaction for this synthesis. Describe the relevant thermodynamic quantities I'll need to compute  $\Delta H_{rxn}^\circ$  at 400K, and write a mathematical expression with these quantities to explicitly show how  $\Delta H_{rxn}^\circ$  at 400 K can be found. You don't have to evaluate the expression but I'm not your mom I'm not gonna tell you what to do.

To compute the enthalpy of reaction at 400 k we'll need the enthalpies of formation of everything involved in the reaction, heats of vaporization for benzene and cyclohexane, the heat capacities of benzene and cyclohexane in both the liquid and gaseous states for each compound, and the heat capacity of  $\text{H}_{2(g)}$ . Notice that I omitted the catalyst from the necessary quantities we'll need. This is because the catalyst appears in the same phase on both sides and therefore won't affect the enthalpy of reaction at all. Also, notice that we're given the enthalpy of reaction for the hydrogenation of benzene to cyclohexane in their liquid states above. So, instead of requiring the heats of formation for each compound we can base our analysis off of the enthalpy of reaction for the liquid phase transformation which affords us no need for knowing the heats of formation for any of the reactants or products.

Figure 6.3 hopefully summarizes what I just said. Thus, an expression for  $\Delta H_{rxn}^\circ$  at 400K is given by

$$\begin{aligned} \Delta \tilde{H}_{rxn}(400 \text{ K}) = & \Delta \tilde{H}_{rxn}^\circ \\ & + \left\{ \int_{298}^{T_{v,benz}} (\tilde{C}_{P,benz} + 3\tilde{C}_{P,H_2} dT) + \Delta \tilde{H}_{vap,benz} + \int_{T_{v,benz}}^{400} (\tilde{C}_{P,benz} + 3\tilde{C}_{P,H_2} dT) \right\} \\ & + \left\{ \int_{298}^{T_{v,cxh}} \tilde{C}_{P,cxh} dT + \Delta \tilde{H}_{vap,cxh} + \int_{T_{v,cxh}}^{400} \tilde{C}_{P,cxh} dT \right\} \end{aligned}$$

where the first term is the heat of reaction for the hydrogenation in the liquid phase, the second term represents

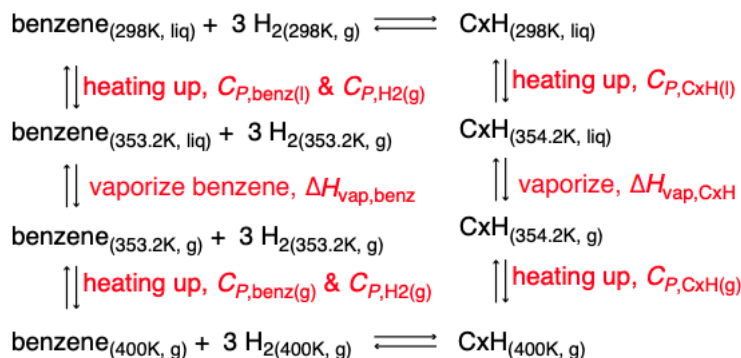


Figure 6.3: Thermodynamic cycle for the proposed hydrogenation of benzene to cyclohexane. Shoutout Dr. Fried for making this graphic.

the contribution from the heating up and vaporization of the reactants, and the third term represents the heating up and vaporization of the product. Also note that I used  $T_{v,X}$  to represent the temperature of vaporization for a species  $X$  cause they weren't given to us.

## 6.2.2 Bond Dissociation Enthalpy

The *bond dissociation enthalpy*<sup>4</sup> (BDE) is the energy needed to break one mole of a bond between atoms to give separated atoms whilst the compound is in a gaseous state. Organic chemists tend to focus more attention on the breaking of specific bonds in a molecule as opposed to creating one from its constituent elements.

BDEs are necessarily positive since breaking bonds requires an input of energy. Interestingly, BDEs are measured using spectroscopic models of bond vibrations, since the reactions are oftentimes too difficult to execute experimentally.<sup>5</sup>

Bond dissociation energies have proven useful in predicting whether a chemical reaction will be enthalpically favorable or not. This is all fine and dandy, however, using BDEs is not always exact because the energy of one sort of bond in a particular molecule will not always be the same as the same type of bond in a different molecule. Why? This is the question that Sidney Benson sought to answer (in the next section, in fact).

Here is a question regarding bond dissociation energies from one of the homeworks that I thought was cool: Consider the possibility that the Cope rearrangement proceeds through a biradical intermediate. We could imagine two such possible pathways, illustrated in Figure 6.4. Evaluate the feasibility of the two mechanisms, based on the following data:

Quantity	kcal/mol
$\Delta H_f^\circ(1,5\text{-hexadiene})$	20.1
$\Delta H_f^\circ(\text{propene})$	4.8
$\Delta H_f^\circ(\text{cyclohexane})$	-29.5
BDE(H-H)	104
BDE(H-propyl)	86.5
BDE(H-cyclohexyl)	95.5

To evaluate the feasibility of each mechanism we can start by computing the enthalpy of formation for the two intermediates. For the top intermediate in Figure 6.4, the heat of formation is going to be a linear combination of the heat of formation for two propene groups, the BDE(H-propyl), and the BDE(H-H) since the H atoms we liberate will react to form  $\text{H}_2$  gas.

<sup>4</sup>The bond dissociation enthalpy can also be referred to as the bond dissociation energy and even just the bond strength. For all intents and purposes, these phrases are interchangeable.

<sup>5</sup>These types of reactions are known as "homolytic cleavages."

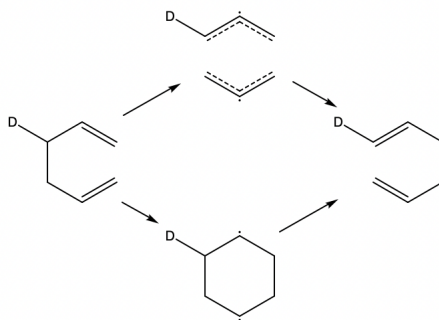


Figure 6.4: Two possible biradical pathways for the Cope rearrangement

Thus, this heat of formation is given by

$$\begin{aligned}
 \Delta H_{f,propenes}^{\circ} &= 2\Delta H_{f,propene}^{\circ} + 2\text{BDE}(\text{H-propyl}) - \text{BDE}(\text{H-H}) \\
 &= 2(4.8) + 2(86.5) - (104) \\
 &= 78.6 \text{ kcal/mol}
 \end{aligned}$$

We can follow a similar procedure to find the heat of formation for the lower intermediate. In this case, the heat of formation will be a linear combination of the heat of formation for a molecule of cyclohexane, the  $\text{BDE}(\text{H-cyclohexyl})$ , and the  $\text{BDE}(\text{H-H})$  for the same reason as above. Thus,

$$\begin{aligned}
 \Delta H_{f,cyclohexane}^{\circ} &= \Delta H_{f,cyclohexyl}^{\circ} + 2\text{BDE}(\text{H-cyclohexyl}) - \text{BDE}(\text{H-H}) \\
 &= (-29.5) + 2(95.5) - (104) \\
 &= 57.5 \text{ kcal/mol}
 \end{aligned}$$

Clearly the formation enthalpies for each of these are very high with respect to the enthalpy of formation for 1,5-hexadiene, coming in at only 20.1 kcal/mol. Thus, we can say with confidence that the biradical intermediate is implausible and the more likely mechanism is the *concerted sigmatropic rearrangement*, which we know to be the case.

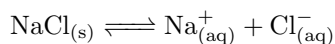
Here's another example, this one being slightly more disconnected from what we just discussed but important nonetheless<sup>6</sup>: A remarkable property of NaCl is that its solubility is essentially constant in temperatures from 0°C to 100°C, going from 370 g/L to 380 g/L over the interval. Explain what this implies about relevant thermodynamic properties for the dissolution of sodium chloride in water and rationalize the result with a molecular-level explanation.

Recall Equation (5.2.8), the van't Hoff equation, which relates the equilibrium constant of a reaction to some relevant thermodynamic quantities:

$$\ln K_{eq} = \frac{-\Delta \tilde{H}_{rxn}^{\circ}}{R} \left( \frac{1}{T} \right) + \frac{\Delta \tilde{S}_{rxn}^{\circ}}{R}$$

We're given that the solubility is unchanging over a temperature range and therefore the equilibrium constant, which can be thought of as a *dissociation constant* in this context, must be unchanging. Hence, the enthalpy of reaction must be zero for the dissolution of sodium chloride in water.

Now, how can we rationalize this result using molecular interactions? First, let's illustrate the transformation that is taking place:



<sup>6</sup>Also I just wasn't really sure where to put this example but I really like the question so I wanted to include it somewhere.

With the enthalpy of reaction being zero we can think of the heats of formation of the reactants and products being equal. Note that crystalline  $\text{NaCl}_{(s)}$  has a very high bond enthalpy associated with the ionic bonds in the lattice and to match this large heat of formation there must be an equally strong enthalpic contribution from solvent-ion interactions in the products. Thus, the solvation energy associated with dissolving the sodium and chloride ions must be equally as strong as the bond enthalpy of the ionic bonds in the lattice of  $\text{NaCl}_{(s)}$ . With all of this in mind it makes sense intuitively that the dissolution of sodium chloride is a primary entropy driven reaction.

### 6.2.3 Benson Group Additivity

*Benson group additivity* uses the experimentally calculated heats of formation for individual groups of atoms to calculate the entire heat of formation for a molecule under investigation<sup>7</sup>. Moreover, using Benson increments can quickly afford an estimate for whether a reaction is endo- or exothermic.

I think the best way to illustrate Benson increments is using an example. Here's one from the homework: Use Benson increments to calculate  $\Delta H_{rxn}^\circ$  for the retro Diels-Alder reaction below, with the values given by the NIST at [this link](#). Also, use the following strain values:

Strain for bicyclo-(4,1,0)-heptane	$\Delta H^\circ = 28.9 \text{ kcal/mol}$
Strain for <i>cis</i> double bond	$\Delta H^\circ = 1.0 \text{ kcal/mol}$

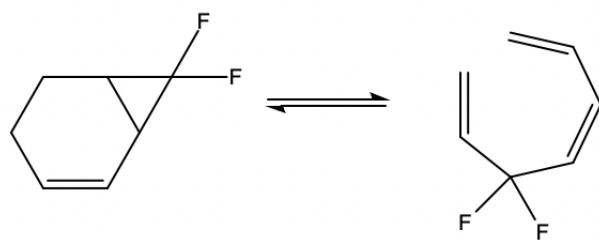


Figure 6.5: Retro Diels Alder Reaction

Note that with the link given we don't have values for  $\text{C}-\text{C}_2\text{F}_2$  or  $\text{F}-\text{C}$ . However, notice that we have bond of the former type and two of the latter type in each structure so that these values would cancel anyways. With this in mind, I won't include any of these terms in the calculation for the heats of formation. Figure 6.6 illustrates the Benson increments for each group on both the reactant and product.

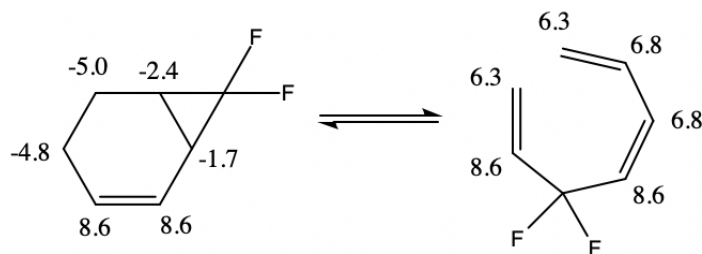


Figure 6.6: Benson increments labeled for each group

Then, proceeding with the calculation, the heat of formation for the reactants is given by (making sure to

<sup>7</sup>Benson increments fall under the umbrella category of *heat of formation group additivity*, a topic which includes all of the methods for calculating the heat of formation of an organic compound based on additivity. Other methods include the Gronert model which is based on not breaking molecules into fragments but instead considering the 1,2- and 1,3- interactions of groups

include the terms for ring strain and *cis* double bonding)

$$\Delta H_{f,reactant}^{\circ} = (-4.8) + (-5.0) + (-2.4) + (-1.7) + 2(8.6) + 28.9 + 1 = 33.2 \text{ kcal/mol}$$

and the heat of formation for the product is given by

$$\Delta H_{f,product}^{\circ} = 2(6.3) + 2(8.6) + 2(6.8) + 1 = 44.4 \text{ kcal/mol}$$

so that the heat of reaction can be computed as

$$\Delta H_{rxn}^{\circ} = 44.4 - 33.2 = 11.2 \text{ kcal/mol}$$



## CHAPTER

# 7

# STATISTICAL MECHANICS

*Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.*

*- Marie Curie*

Statistical mechanics spans a much broader, intellectually challenging, and mathematically rigorous field than I cover here. I'll try to talk about things that I find cool that are even somewhat related to what Dr. Fried asks of his students but not covered in class but I implore anyone who's interested to read more on the subject.

The science of statistical mechanics has the special function of providing reasoning for treating the behavior of mechanical systems under circumstances such that our knowledge of the condition of the system is less than the theoretically possible maximum. That is, it allows us to make good guesses. Since our knowledge of the physical world and thermodynamic systems is such that we can never know *everything* about the system, statistical mechanics provides significant supplementation to ordinary mechanics, which is abstract at best when it comes to *real* systems. Stated in another way, the transition from knowing exactly what is going on to knowing only the probability of exactly what is going on is the same transition from mechanics to statistical mechanics. With these key ideas lurking in the background we'll begin to analyze the general structure of statistical mechanics, beginning with the *ensemble approach*.

An ensemble is a large collection of trajectories of a system, considered all at once, each of which represents a possible state the system might be in. A *thermodynamic ensemble* is a specific variety of ensemble that is in statistical equilibrium and is used to derive the properties of thermodynamic systems from the laws of classic and/or quantum mechanics.

For our purposes, the ensemble method will provide a means of accessing bulk thermodynamic properties from molecular models. On their own, molecular models tell us nothing about the equilibrium distribution of thermodynamic properties and instead provide a comprehensive list of allowed microstates of a system.

The beauty of using ensembles instead of computation-intensive simulations<sup>1</sup> is in our ability to calculate the average thermodynamic properties of a system by averaging across the different trajectories (mentioned

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<sup>1</sup>Running simulations for a system involves determining (arbitrary) initial conditions, defining potential functions, evaluating the instantaneous forces on each particle at the system at all times in the interval, and generating new conditions from these forces. With modern technology simulations can be very intuitive and visualized with relative ease. However, they require many calculations and were not possible until very recently. Hence the creation of the ensemble method.

above) within our ensemble. This “convergence” to the time averages is made possible by the *Ergodic hypothesis*,<sup>2</sup> which formally states that ensemble averages are equal to time averages,

$$\langle A \rangle \equiv \frac{1}{N} \sum_{i=1}^N A_i = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(t) dt \quad (7.0.1)$$

where  $A_i$  is some measure of the system, and  $N$  is the number of trajectories we consider in the system. Phrased slightly differently, the Ergodic hypothesis posits that the average of microstates taken at different times from a single system can be replaced with the average of microstates taken from many trajectories of the same system, taken at an arbitrary time.

The central idea behind Ergodic theory is that any single trajectory within an ensemble will eventually pass through all accessible trajectories possible in the system. For example, this would imply that if we looked at a gas particle restricted to a box of a finite volume then the particle would eventually occupy every single accessible point in space within the box. Unfortunately, not many systems are strictly ergodic, hence the “Ergodic hypothesis”.

There are two important differences that make dealing with ensembles easier than simulations:

1. The ensemble has no concept of time.
2. We can *predict* many properties about an ensemble (in the form of ensemble-averaged properties) starting from a potential function (for thermodynamic systems these are states and energies) and without necessarily simulating the dynamics.

Based on what we’ve read so far, ensembles seem like the clear winner when choosing a method of trying to connect the microscopic properties of a system to the macroscopic ones through statistical mechanics. However, there are some aspects of our assumptions about ensembles that we need to keep in mind when choosing the trajectories of the system to represent the ensemble.

Firstly, for ensemble-averages to accurately reflect real, observed properties, the number of times a given microstate appears in the ensemble (i.e., its *weight*) must be directly proportional to the amount of time the system would spend in that microstate. Then, the challenge is to ensure we include each microstate *the right number of times*. How then can we populate an ensemble without explicitly looking at the simulation? That’s a good question.

## 7.1 Extensive and Intensive Properties

[https://scholar.harvard.edu/files/schwartz/files/8-freeenergy\\_0.pdf](https://scholar.harvard.edu/files/schwartz/files/8-freeenergy_0.pdf)

## 7.2 The Microcanonical (NVE) Ensemble

We’ll now consider the simplest case of an isolated system. Then, we have a well-defined number of molecules ( $N$ ) in the system as well as a constant volume ( $V$ ) and energy ( $E$ ). In creating the ensemble we’ll choose  $m$  trajectories of the system so that each trajectory corresponds to one of  $m$  different microstates. Logic insists that if all  $m$  microstates have equal energy then in theory they should be equiprobable (or in the words of Dr. Fried, they’re *a priori equally likely*). Let  $N_i$  represent the  $i$ th microstate and let  $\mathbb{A}$  represent the total number of microstates in our ensemble so that

$$\sum_{i=1}^m N_i = \mathbb{A} \quad (7.2.1)$$

<sup>2</sup>The Ergodic hypothesis is part of *Ergodic theory*, which is the study of systems possessing the property that given enough time, all points within a system will eventually visit all parts of the space that the system exists in. This theory implies that the average behavior of a system can be deduced from the “trajectory” of a normal point, exactly as we’ve postulated above. This property is known as *ergodicity* and is pretty cool.

where the probability of being in a particular microstate  $p_i$  is given by,

$$p_i = \frac{N_i}{\mathbb{A}} \quad (7.2.2)$$

(sometimes referred to as the “case of equally likely outcomes”).

Now let’s shift our attention to the ways of assigning trajectories to this system, i.e., choosing the total number of ways we could have selected  $N_1, \dots, N_m$  from the  $\mathbb{A}$  total number of microstates. This is given by the multinomial coefficient:

$$\binom{\mathbb{A}}{N_1, \dots, N_m} = \frac{\mathbb{A}!}{N_1! \dots N_m!}$$

Now that we have a representation of the number of microstates  $W$  of the system, the most probable state of the system is the one which maximizes  $W$ . This is tantamount to asking, which value of  $W$  maximizes  $S = k_B \ln W$ ?<sup>3</sup> Recall that for an isolated system, entropy is an indicator of spontaneity. So, the intuition behind maximizing entropy should make sense in the context of trying to find the most probable state of the system at equilibrium. In the above representation for  $W$ , apply Stirling’s approximation:

$$\ln W = \mathbb{A} \ln \mathbb{A} - \sum_{i=1}^m N_i \ln N_i$$

The algebra is omitted here because a) it’s lame and b) it’s pretty simple.

Now for the fun part: Notice that we could increase  $W$  with ease by simply having a larger ensemble. So, let’s assume that we have a fixed number of microstates in the ensemble so that  $\mathbb{A}$  is constant. Furthermore, notice that  $W$  is a function of  $m$  variables, all of the  $N_i$ ’s (the  $\mathbb{A}$  is fixed number, as mentioned literally 2 seconds ago how did you already forget smh) constrained to the condition that  $\mathbb{A} = \sum_{i=1}^m N_i = \text{const}$ . Hence, we invoke (enter stage left) *the Lagrangian*:

$$\mathcal{L}(\vec{x}, \vec{\lambda}) = f(\vec{x}) - \sum_{i=1}^c \lambda_i g_i(\vec{x}) \quad (7.2.3)$$

If you’ve taken Calc III, skip this paragraph. The method of Lagrange multipliers utilizes the fact that for the level sets of a  $n$ -dimensional function, the gradient (a fancy word for the vector of partial derivatives for a function of more than one variable) of the function is *always perpendicular* to the level sets. Hence, when the function we are trying to optimize ( $f(\vec{x})$  above) is along the constraint function ( $g(\vec{x})$  above) their gradients will be parallel. But Sam, I don’t see any gradients above, what’s up with that? Not only is that a fantastic observation, but also it segways greatly into the following point: We’re trying to *optimize* the function  $f$  above, so let’s find the gradient and set it equal to zero (just as we would in single-variable calc):

$$\begin{aligned} 0 &= \nabla f(\vec{x}) - \nabla \left( \sum_{i=1}^c \lambda_i g_i(\vec{x}) \right) \\ \nabla f(\vec{x}) &= \nabla \left( \sum_{i=1}^c \lambda_i g_i(\vec{x}) \right) \\ \nabla f &= \lambda \nabla g \end{aligned}$$

The last equation (hopefully) looks familiar if you’ve taken Calc III. Thus, for a system of  $m$  variables (like the

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<sup>3</sup>Note that we have this relationship between maximizing  $W$  and  $S$  because the natural logarithm is a monotonically increasing function.

one we began with), we're left with a *system* of equations of the form

$$\begin{aligned}\frac{\partial f}{\partial x_1}(\vec{x}) &= \lambda_1 \left( \frac{\partial g}{\partial x_1}(\vec{x}) \right) \\ \frac{\partial f}{\partial x_2}(\vec{x}) &= \lambda_2 \left( \frac{\partial g}{\partial x_2}(\vec{x}) \right) \\ &\vdots \\ \frac{\partial f}{\partial x_m}(\vec{x}) &= \lambda_m \left( \frac{\partial \vec{g}}{\partial x_m}(\vec{x}) \right)\end{aligned}$$

alongside the initial constraint function (which I didn't rewrite above)<sup>4</sup>.

Now, how can we apply the Lagrangian to the microcanonical ensemble? Notice that the function we are trying to optimize (in particular, maximize) is  $\ln W$  while we're constrained to the fact that  $\mathbb{A} = \text{const}$ . So, in the example above we have  $f \sim \ln W$  and  $g \sim \mathbb{A}$ . Then, we are left with

$$\begin{aligned}\mathcal{L}(\vec{x}, \vec{\lambda}) &= \ln W - \lambda \sum_{i=1}^m \mathbb{N}_i \\ &= \nabla \left( \mathbb{A} \ln \mathbb{A} - \sum_{i=1}^m \mathbb{N}_i \ln \mathbb{N}_i \right) - \lambda \nabla \left( \sum_{i=1}^m \mathbb{N}_i \right) \\ \nabla \left( \mathbb{A} \ln \mathbb{A} - \sum_{i=1}^m \mathbb{N}_i \ln \mathbb{N}_i \right) &= \lambda \nabla \left( \sum_{i=1}^m \mathbb{N}_i \right)\end{aligned}$$

To simplify our lives let's first differentiate only one of these elements on the left-hand side with respect to some  $\mathbb{N}_i$  and determine what the partial derivatives look like:

$$\begin{aligned}\frac{\partial}{\partial \mathbb{N}_i} \left( \mathbb{A} \ln \mathbb{A} - \mathbb{N}_i \ln \mathbb{N}_i \right) &= \left( \frac{\partial \mathbb{A}}{\partial \mathbb{N}_i} \ln \mathbb{A} + \mathbb{A} \frac{\partial \ln \mathbb{A}}{\partial \mathbb{N}_i} \right) - \left( \frac{\partial \mathbb{N}_i}{\partial \mathbb{N}_i} \ln \mathbb{N}_i + \mathbb{N}_i \frac{\partial \ln \mathbb{N}_i}{\partial \mathbb{N}_i} \right) \\ &= \ln \mathbb{A} + \mathbb{A} \frac{1}{\mathbb{A}} - \ln \mathbb{N}_i + \mathbb{N}_i \frac{1}{\mathbb{N}_i} \\ &= \ln \mathbb{A} - \ln \mathbb{N}_i \\ &= \ln \left( \frac{\mathbb{A}}{\mathbb{N}_i} \right)\end{aligned}$$

For the derivation above, recall that  $\mathbb{A} = \sum_{i=1}^m \mathbb{N}_i$  so that  $\partial \mathbb{A} / \partial \mathbb{N}_i = 1$ . Now, let's relate this to our Lagrange equation above:

$$\begin{aligned}\nabla \left( \mathbb{A} \ln \mathbb{A} - \sum_{i=1}^m \mathbb{N}_i \ln \mathbb{N}_i \right) &= \lambda \nabla \left( \sum_{i=1}^m \mathbb{N}_i \right) \\ \ln \left( \frac{\mathbb{A}}{\mathbb{N}_i} \right) &= \lambda \frac{\partial}{\partial \mathbb{N}_i} \left( \mathbb{N}_i \right) \\ \ln \left( \frac{\mathbb{A}}{\mathbb{N}_i^*} \right) &= \lambda \\ \frac{\mathbb{N}_i^*}{\mathbb{A}} &= \frac{1}{e^\lambda}\end{aligned}\tag{7.2.4}$$

Here,  $\mathbb{N}_i^*$  denotes the set of  $\mathbb{N}_i$  which maximize  $W$ . Awesome! Recall two things: 1) We have  $m$  equations of this form for each  $\mathbb{N}_i$  and 2) each of the  $m$  equations will look the exact same because we derived this result

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<sup>4</sup>More generally, optimizing a nonlinear function with a set of constraints which are *inequalities* instead of *equalities* requires satisfying the *Karush-Kuhn-Tucker* conditions, a set of optimality conditions which are useful in finding the minima of such systems. This could not be less related to this class, however, I just took my intro to optimization final and the KKT conditions are all I can think about.

using an arbitrary  $N_i$ . Then, summing each of these equations affords

$$\frac{N_1^*}{\mathbb{A}} + \frac{N_2^*}{\mathbb{A}} + \cdots + \frac{N_m^*}{\mathbb{A}} = \frac{\mathbb{A}}{\mathbb{A}} = 1 = me^{-\lambda}$$

$$m = e^{\lambda}$$

Now, returning to our  $m$  equations, recall that  $p_i = N_i/\mathbb{A}$  for any given  $i$  so that  $p_i = 1/m$  by Equation (7.2.4). This result is uber important: *In the beginning of this derivation we postulated that each the microstates was equiprobable; here we proved it.* Not only is this the most probable ensemble, but later we'll come to realize that this is the *only possible* ensemble.

An interesting connection between this derivation and the macroscopic world is in the limit as  $\mathbb{A}$  tends to infinity. As the number of possible trajectories increases (that is,  $m$  increases; this is the quantity we constrained to a constant earlier), the probability that a particular microstate effectively decreases so that the distributions of each particular  $N_i$  becomes more tightly peaked. Hence, we view macroscopic systems as “ordered,” even when their underlying molecular descriptions are immensely chaotic.

With this critical fact derived, let's derive some terms and organize our results:

- $p_i = \frac{1}{e^{\lambda}} = \frac{1}{m}$  is the *population* of the  $i$ th microstate, which is equivalent to the probability of occupying a particular microstate in this ensemble.
- $\Omega = e^{\lambda} = m$  is the *Microcanonical partition function*. It illustrates all of the possible microstates possible in the system.
- $S = k_B \ln \Omega$  is the entropy of the microcanonical ensemble.

### 7.2.1 The Microcanonical Ensemble for an Ideal Gas

So far we've considered an ensemble for a discrete number particles. Now, we'll analyze the mechanics of an ideal gas.

Consider a collection of  $N$  gas particles, each of which has 3 degrees of freedom (movement in the  $x$ ,  $y$ , and  $z$  directions). Then, we can express the total energy of the system as,

$$E = \text{PE} + \text{KE} = 0 + \sum_{i=1}^{3N} \frac{1}{2} m_i v_i^2 = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} \quad (7.2.5)$$

that is, all of the energy is in the form of kinetic energy. Furthermore, suppose that this gas is isolated so that the energy of the system can be considered constant and all microstates have the same energy.

How can we express the number of microstates of the system? Firstly, consider a single atom of ideal gas: The energy of this atom is given by

$$E = \frac{p^2}{2m} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$p_x^2 + p_y^2 + p_z^2 = 2mE \quad (7.2.6)$$

Notice that this equation is in the form of a 3-dimensional sphere with radius  $\sqrt{2mE}$ . Thus, each point on the “surface” of this sphere (“surface” is in quotes here because it's not technically a sphere, but it makes our life easier thinking about this situation in terms of a sphere) has an equal weight in the ensemble and all points off the surface have zero weight in the ensemble.

Above we considered a single atom of an ideal gas with 3 translational degrees of freedom which afforded momentum in the  $x$ ,  $y$ , and  $z$  directions,  $p_x$ ,  $p_y$ , and  $p_z$ , respectively. However, we also must specify the *coordinates* of that atom,  $x$ ,  $y$ , and  $z$ . Then, each microstate is defined by 6 points and therefore lives in 6-dimensional space, as opposed to 3-dimensions. Additionally, recall that each microstate of this system that

has weight in the ensemble must lie on the “shell” corresponding to a specific amount of energy  $E$ . Then, if we integrate over each coordinate of the system over the entire phase space,

$$\Omega(E) = \int_E dx_1 dy_1 dz_1 \dots dz_N dp_{x_1} dp_{y_1} \dots dp_{z_N} \quad (7.2.7)$$

Above we considered the phase space  $\Omega$  as being a shell of energy, in particular an  $n$ -dimensional sphere. Most of the time we’re interested in an infinitesimally small section of the sphere, one that represents only a specific amount of energy  $E$ . We can restrict atoms to this particular energy value by assigning some  $E^*$  and  $E^* + \delta E^*$  to bound the specific energy  $E$  that we’re interested in. Then,

$$\Omega(E)\delta E = \int_{E^* < E < E^* + \delta E} dx_1 dy_1 dz_1 \dots dz_N dp_{x_1} dp_{y_1} \dots dp_{z_N} \quad (7.2.8)$$

represents the shell of energy corresponding to a *specific* energy level.

Notice that part of the integral in Equations (7.2.7) and (7.2.8) returns the volume of a  $3N$ -dimensional sphere (there are  $N$  sets of 3 positional coordinates  $x$ ,  $y$ , and  $z$ . This convention temporarily ignores the momenta terms). Lucky for us, people smarter than us already computed an explicit formula for an  $n$ -dimensional sphere:

$$V_n(R) = \frac{\pi^{n/2} R^n}{(\frac{n}{2})!}$$

Here,  $R$  is the radius of the sphere. Recall that above we already defined the radius of our sphere as  $\sqrt{2mE}$ . This formula will allow us to calculate the volume of a thin shell of momenta space that corresponds to the total energy at the specific point on the sphere  $E$  that we’re interested in.

To begin that calculation let’s break up the integral above (in the manner that I’ve already hinted at):

$$\begin{aligned} \Omega(E)dE &= \left( \int_{E^* < E < E^* + dE} dx_1 dy_1 dz_1 \dots dz_N \right) \left( \int_{E^* < E < E^* + dE} dp_{x_1} dp_{y_1} dp_{z_1} \dots dp_{z_N} \right) \\ &= dV_{3N} + \int_{E^* < E < E^* + dE} dp_{x_1} dp_{y_1} dp_{z_1} \dots dp_{z_N} \end{aligned}$$

The  $dV_{3N}$  term is in fact a change because we are looking at the integral on  $E^* < E < E^* + \delta E$  which has an inherent change. Thus, we can compute the total energy at on the particular shell of energy  $E$  in momenta space as

$$\begin{aligned} \Omega(E) &= \frac{dV_{3N}(\sqrt{2mE})}{dE} \\ &= \frac{d}{dE} \left( \frac{\pi^{3N/2} (\sqrt{2mE})^{3N}}{(\frac{3N}{2})!} \right) \\ &= \frac{\pi^{3N/2} [3Nm(2mE)^{\frac{3N}{2}-1}]}{(\frac{3N}{2})!} \\ &= \frac{3Nm\pi^{3N/2} R^{3N-2}}{(\frac{3N}{2})!} \end{aligned} \quad (7.2.9)$$

where  $R = \sqrt{2mE}$  is the radius of the sphere.

At this point we shift our attention and ask an interesting question about the collection of particles we’ve been studying: What is the probability that a particular atom will have a given amount of momentum,  $p_1$ , in the  $z$  direction? For a single atom system, this probability is proportional to the area of the circular annulus elevated  $p_1$  along the  $z$ -axis from the center of the sphere. To compute this we’ll be interested in the area bounded by two circles which lie along arbitrarily close to one another on the sphere, one of radius  $R = \sqrt{2mE}$  and the other of radius  $r = \sqrt{2m(E + dE)}$ . Notice that this new radius  $r$  can be equivalently expressed as  $r = \sqrt{2mE - p_1^2}$  using the fact that the probability is proportional to the area of the annulus mentioned

above and the Pythagorean Theorem. Now, we'll compute the area of this annulus in a similar fashion as the volume of the sphere itself. Note that since the sphere lived in  $3N$ -dimensional space, the annulus lives in  $(3N - 1)$ -dimensional space (which I think is intuitive enough).

$$\begin{aligned}
\frac{\text{area of annulus}}{dE} &= \frac{dV_{3N-1}(\sqrt{2mE - p_1^2})}{dE} \\
&= \frac{d}{dE} \left( \frac{\pi^{(3N-1)/2} (\sqrt{2mE - p_1^2})^{3N-1}}{(\frac{3N-1}{2})!} \right) \\
&= \frac{\pi^{(3N-1)/2} [(3N-1)m(2mE - p_1^2)^{\frac{3N-1}{2}-1}]}{(\frac{3N-1}{2})!} \\
&= \frac{(3N-1)m\pi^{(3N-1)/2} r^{3N-3}}{(\frac{3N-1}{2})!} \tag{7.2.10}
\end{aligned}$$

The probability density of being in the particular annulus (above) is the area of said annulus, Equation (7.2.10), divided by the total volume of the shell, Equation (7.2.9). Thus,

$$\begin{aligned}
f(p_1) &= \frac{\text{area of annulus}}{\text{volume of sphere}} \\
&= \frac{(3N-1)m\pi^{(3N-1)/2} r^{3N-3}}{(\frac{3N-1}{2})!} \left( \frac{3Nm\pi^{3N/2} R^{3N-2}}{(\frac{3N}{2})!} \right)^{-1} \\
&\vdots \\
&= \frac{R^2}{r^3} \left( 1 - \frac{p_1^2}{2mE} \right)^{3N/2} \tag{7.2.11}
\end{aligned}$$

Briefly, let's considering the feasibility of our result. The factor inside the parentheses is taken to an enormous power, on the order of  $N$ . Thus,

$$1 - \frac{p_1^2}{2mE} \approx 1$$

otherwise, the entire expression in (7.2.11) would vanish. Moreover, notice that

$$1 \approx 1 - \frac{p_1^2}{2mE} = \frac{2mE - p_1^2}{2mE} = \left( \frac{\sqrt{2mE - p_1^2}}{\sqrt{2mE}} \right)^2 = \frac{r^2}{R^2} \Rightarrow r \approx R$$

and that we can approximate

$$1 - \frac{p_1^2}{2mE} \approx \exp \left\{ - \frac{p_1^2}{2mE} \right\}$$

for small enough values in the exponent (check for yourself that this is true). Thus, we can make the following approximation:

$$\begin{aligned}
\frac{R^2}{r^3} \left( 1 - \frac{p_1^2}{2mE} \right)^{3N/2} &\approx \frac{1}{r} \left( \exp \left\{ - \frac{p_1^2}{2mE} \right\} \right)^{3N/2} \\
&= \frac{1}{\sqrt{2mE}} \left( \exp \left\{ - \frac{1}{2} \left( \frac{3Np_1^2}{2mE} \right) \right\} \right)
\end{aligned}$$

Notice that this is (nearly) a Gaussian distribution with mean zero and standard deviation  $\sqrt{2mE/3N}$ . The only thing left to do to afford our probability density for  $p_1$  is to normalize this expression:

$$f(p_1; E, N, m) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp \left\{ - \frac{p_1^2}{2m} \frac{3N}{2E} \right\} \tag{7.2.12}$$

Alright that was a lot of math, even for me. Let's take a quick H<sub>2</sub>O break, maybe grab a snack, and regroup in 5.

We're back. Let's consider the implications of our derivation above:

1. We were able to solve the momentum distribution for any particle without solving any equations of motion.
2. We've found that the momentum distribution is extremely tightly peaked. In fact, most of the momenta will be found within one standard deviation of the center of the distribution, that is, within  $\sqrt{2mE/3N}$  which is tiny compared to the total possible values of momenta,  $\sqrt{2mE}$ . Intuitively, this result makes sense: As we increase the number of particles in our system, by the law of large numbers, the average momentum limits towards a fixed value.

A major implication of our derivation that is deserved of more than just a bullet point is that it *affords the internal energy for an ideal gas*. Suppose that we choose to substitute  $3N/2E = 1/k_B T$  (do these quantities have the same physical meaning? i.e., do they have the same units?) to afford an expression for the energy  $E$ ,

$$\frac{3N}{2E} = \frac{1}{k_B T} \Rightarrow E = \frac{3}{2} N k_B T = \frac{3}{2} RT$$

which is exactly the familiar representation for the internal energy of an ideal gas.

Another major implication of our derivation is that it *affords the ideal gas law*. Suppose we want to find the average amount of (kinetic) energy of the particles in this collection. This is equivalent to calculating the weighted average of the kinetic energies over all possible momenta (i.e., using the function we just defined):

$$\begin{aligned} KE_{avg} &= \int_{-\infty}^{\infty} \left( \frac{p_1^2}{2m} \right) f(p_1) dp_1 \\ &= \int_{-\infty}^{\infty} \left( \frac{p_1^2}{2m} \right) \frac{\exp\left\{ \frac{-p_1^2}{2m} \frac{3N}{2E} \right\}}{\sqrt{2\pi m(2E/3N)}} dp_1 \\ &= \frac{1}{2m\sqrt{2\pi m k_B T}} \int_{-\infty}^{\infty} p_1^2 \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} dp_1 \end{aligned}$$

This integral is not at all trivial and in the lecture slides Dr. Fried omits the entire evaluation because this is a physical chemistry class and not a vector calculus class. I, however, think the derivation is more than worthy enough of being shown off in all its glory. Moreover, I'll integrate the function in more than one way: Firstly, let's rearrange the integral above (omitting the constants, for brevity) as follows:

$$\int_{-\infty}^{\infty} p_1 \left( p_1 \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} \right) dp_1$$

Now, allow  $u = p$  and  $dv = p_1 \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\}$  so that we can integrate by parts with  $du = dp$  and  $v = -mk_B T \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\}$ :

$$\begin{aligned} \int_{-\infty}^{\infty} p_1 \left( p_1 \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} \right) dp_1 &= \left[ -p_1 m k_B T \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} \right]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} -m k_B T \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} dp \\ &= 0 + m k_B T \int_{-\infty}^{\infty} \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} dp_1 \end{aligned}$$

The integral that remains is a *Gaussian integral* and has a known value. The derivation is really cool, involving a change of variables and some cheeky intuition. I'm not gonna derive it here, but I provide the derivation in Section ?? if you're interested. Using this known value, we find

$$m k_B T \int_{-\infty}^{\infty} \exp\left\{ \frac{-p_1^2}{2m k_B T} \right\} dp_1 = m k_B T \sqrt{2\pi m k_B T} = \sqrt{2\pi} (m k_B T)^{3/2}$$

and remembering that I omitted the constants in front of this integral in the first place for brevity, we have



that

$$KE_{avg} = \frac{1}{2m\sqrt{2\pi mk_B T}} \sqrt{2\pi}(mk_B T)^{3/2} = \frac{1}{2}k_B T \quad (7.2.13)$$

which represents the *average amount of energy carried by a translational degree of freedom for a particle*. This result is known as *equipartition*. Additionally, it agrees with what we know already about the internal energy for an ideal gas: First, recall that  $N_A k_B = R$  for a single particle. Then, notice that each particle of an ideal gas has three translational degrees of freedom (in accordance with the three dimensions of motion) so that the internal energy of a *single* particle is given as

$$U = \frac{3}{2}RT$$

and the internal energy for  $n$  moles of an ideal gas is given by

$$U = \frac{3}{2}nRT$$

Awesome!

Before utilizing this result, here's another way of evaluating the integral that gave us some trouble: Let's start by rearranging, this time in a slightly different way:

$$\int_{-\infty}^{\infty} p_1^2 \exp\left\{\frac{-p_1^2}{2mk_B T}\right\} dp_1 = \int_0^{\infty} p_1 \exp\left\{\frac{-p_1^2}{2mk_B T}\right\} 2p_1 dp_1$$

Above we shifted the lower limit of integration up to 0 since the function is completely nonnegative. At the same time, we doubled the value of the integral to account for negative momenta which are lost when we begin integration at 0. This factor of 2 was brought inside the integral, affording the  $2p_1 dp_1$  term. At this point, we can make the variable substitution  $u = p_1^2/(2mk_B T)$  so that  $du = 2p_1 dp_1/(2mk_B T)$  which simplifies our integral as

$$\int_0^{\infty} p_1 \exp\left\{\frac{-p_1^2}{2mk_B T}\right\} 2p_1 dp_1 = \int_0^{\infty} (2mk_B T u)^{1/2} e^{-u} (2mk_B T du)$$

which can be evaluated with the Gamma function:

$$\begin{aligned} \int_0^{\infty} (2mk_B T u)^{1/2} e^{-u} (2mk_B T du) &= \sqrt{2}(mk_B T)^{3/2} \Gamma\left(\frac{3}{2}\right) \\ &= (2mk_B T)^{3/2} \frac{\sqrt{\pi}}{2} \\ &= \sqrt{2\pi}(mk_B T)^{3/2} \end{aligned}$$

Plugging this result back into our original expression:

$$KE_{avg} = \frac{1}{2m\sqrt{2\pi mk_B T}} \sqrt{2\pi}(mk_B T)^{3/2} = \frac{1}{2}k_B T$$

which agrees exactly with our result from before.

Now, onto deriving the ideal gas law. Somehow we need to relate the average amount of energy we considered above to the pressure and volume of a container holding an ideal gas. Let's consider the momentum of a particle in this collection: Pressure is a result of molecules colliding with a surface (in this case the wall of the container). For an ideal gas, the collisions will be entirely elastic so that the change in momentum will be given by:

$$\Delta \vec{p} = \vec{p}_f - \vec{p}_i = 2\vec{p}$$

Since collisions are elastic and the components of  $\vec{p}_f$  are directed antiparallel to the components of  $\vec{p}_i$ ,  $\vec{p}_f = -\vec{p}_i$  which explains the result above. Considering a short time interval where we measure the number of particles

which collide with the wall, only those particles which are within

$$\Delta \vec{x} = \vec{v} \Delta t = \frac{\vec{p}}{m} \Delta t$$

will hit the container and be transfer momentum. Then, the total momentum transfer to the wall is given by

$$\Delta \vec{p}_{tot} = \int_0^\infty f(p) \left( \frac{N}{V} \right) \left( \frac{\vec{p}}{m} \Delta t \right) (\text{Area}) 2\vec{p} dp$$

where  $f(p)$  is the probability distribution of the momentum we derived above,  $N/V$  accounts for the total number of particles per volume of the container (as to not scale our answer by an unnecessary factor), Area is the area of the container which particles are colliding with,  $2\vec{p}$  is the change in momentum we illustrated above, and we're integrating over all particles with momenta in the direction of the wall (hence only positive values. We could have elected to include "negative" momenta which aren't directed toward the wall and range from negative to positive infinity. This point is remedied later). Before evaluating this integral recall that

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\Delta \vec{p}}{\Delta t \times \text{Area}}$$

so that our integral and can be rearranged and evaluated as follows:

$$\begin{aligned} \frac{\Delta \vec{p}_{tot}}{\Delta t \times \text{Area}} &= \frac{2N}{V} \int_0^\infty f(p) \frac{(\vec{p})^2}{m} d\vec{p} \\ P &= \frac{2N}{V} \left( \frac{1}{2} k_B T \right) = \frac{N k_B T}{V} \\ PV &= RT \end{aligned}$$

In the second step we obtain the same result as we did in the prior derivation. Note that although there isn't a factor of one-half in the integral above, we're only integrating over half of the support as we did in the derivation for Equation (7.2.13) hence the factor of one-half in the answer.

Sam! This isn't the ideal gas law! Might I say that that is an apt observation. Recall that the momentum distribution we've been considering up until this point was for a *single particle*. So, for a mole of particles, we have that  $PV = nRT$  as desired.

### 7.3 The Canonical (NVT) Ensemble

The canonical ensemble describes a system that can exchange heat with a thermal reservoir (in other words, the ensemble is in thermal equilibrium with the reservoir) and therefore energy is *not* conserved in the system. Therefore, microstates will differ in energy. We can justify this observation by saying that lower energy microstates have "donated" their energy to the reservoir while high energy states have "borrowed" energy instead. Moreover, each replica in the ensemble has a fixed number of particles and fixed volume. As before, our goal in constructing an ensemble is to determine the appropriate weight (or contribution) that each microstate plays in the particular macrostate of the system.

Similar to the microcanonical ensemble we'll be interested in finding the weights of each microstate which maximize  $S \sim \ln W$  given

$$W(\mathbb{N}_i; \mathbb{A}) = \binom{\mathbb{A}}{\mathbb{N}_1, \dots, \mathbb{N}_m} = \frac{\mathbb{A}!}{\mathbb{N}_1! \dots \mathbb{N}_m!}, \quad \ln W = \mathbb{A} \ln \mathbb{A} - \sum_{i=1}^m \mathbb{N}_i \ln \mathbb{N}_i$$

with  $\sum_{i=1}^m \mathbb{N}_i = \text{constaint}$ . This time, however, instead of maximizing  $\ln W$  we'll explicitly maximize  $S = k_B \ln W$  and instead of solving for the extensize variables  $\mathbb{N}_i$  (which sum to  $\mathbb{A}$ ) we will solve for the intensive microstate probabilities,  $p_i$  (which sum to 1).

In addition, since the energy is not being conserved within the ensemble, we have a new constraint,

$$U \equiv \sum_{i=1}^m p_i E_i \quad (7.3.1)$$

where  $U$  is the total internal energy of the system,  $E_i$  is the  $i$ th energy of the particle in the ensemble, and  $p_i$  is the probability particle  $i$  obtains that energy. By the first law of thermodynamics, all of the energies in the system must sum to a constant, in particular the total internal energy of the system. If we were to express this energy constraint as an extensive variable, that is, representing the extensive energy of the entire ensemble<sup>5</sup>, we have

$$\mathbb{A}E = \sum_{i=1}^m \mathbb{A}p_i E_i \Rightarrow E_T = \sum_{i=1}^m \mathbb{N}_i E_i$$

as our second constraint.

With these two constraints defined and keeping in mind that we are trying to maximize  $S = k_B \ln W$ , our system of Lagrange multipliers becomes

$$\nabla \left( k_B \ln W \right) = \lambda \left( \sum_{i=1}^m p_i \right) + \beta \left( \sum_{i=1}^m p_i E_i \right)$$

where the right-hand side is the entropy (which we are trying to maximize), the left hand side contains those terms which constrain the function, defined above, and we are differentiating all terms with respect to the  $i$ th probability,  $p_i$ . Before continuing recall that we can express the entropy as *Gibbs entropy*, given as

$$S = -k_B \sum_{i=1}^m p_i \ln p_i$$

so that we can evaluate the Lagrangian equation above, considering just a single  $p_i$  at first and generalizing after:

$$\begin{aligned} \nabla \left( -k_B p_i \ln p_i \right) &= \nabla(\lambda p_i) + \nabla(\beta p_i E_i) \\ -k_B \left( \ln p_i + \frac{p_i}{p_i} \right) &= \lambda + \beta E_i \\ \ln p_i + 1 &= \frac{\lambda + \beta E_i}{k_B} \\ p_i &= \exp \left\{ \frac{-k_B + \lambda + \beta E_i}{k_B} \right\} \end{aligned} \quad (7.3.2)$$

Here we can use on of our constraints. We know that the sum of all the probabilities must be 1 (otherwise we wouldn't have a probability space) and therefore

$$\begin{aligned} 1 &= \sum_{i=1}^m \exp \left\{ \frac{-k_B + \lambda + \beta E_i}{k_B} \right\} \\ &= \exp \left\{ \frac{-k_B + \lambda}{k_B} \right\} \sum_{i=1}^m \exp \left\{ \frac{\beta E_i}{k_B} \right\} \\ &= Q \exp \left\{ \frac{-k_B + \lambda}{k_B} \right\} \end{aligned}$$

---

<sup>5</sup>This is *not* the same as the total internal energy because  $U$  is representative of the system and surroundings, not just the system.

where  $Q$  is the *canonical partition function*<sup>6</sup>. For now, though, we'll use it to isolate  $\lambda$ :

$$\begin{aligned}\frac{1}{Q} &= \exp\left\{\frac{-k_B + \lambda}{k_B}\right\} \\ \ln\left(\frac{1}{Q}\right) &= \frac{-k_B + \lambda}{k_B} \\ -\ln Q &= \frac{-k_B + \lambda}{k_B} \\ \lambda &= -k_B \ln Q + k_B\end{aligned}$$

We can plug this result for  $\lambda$  back into Equation (7.3.2) to afford an expression for the  $i$ th probability,  $p_i$ , in terms of the unknown  $\beta$ :

$$\begin{aligned}p_i &= \exp\left\{\frac{-k_B - k_B \ln Q + k_B + \beta E_i}{k_B}\right\} \\ &= \exp\left\{\frac{-k_B \ln Q + \beta E_i}{k_B}\right\} \\ &= \frac{\exp\left\{\frac{\beta E_i}{k_B}\right\}}{Q}\end{aligned}\tag{7.3.3}$$

Equation (7.3.3) looks promising, as it expresses a *Boltzmann factor*<sup>7</sup> normalized by some partition function  $Q$ .

All that's left is for us to find the parameter  $\beta$ . So, we'll return to entropy, in particular the Gibbs entropy:

$$\begin{aligned}S &= -k_B \sum_{i=1}^m p_i \ln p_i \\ &= -k_B \sum_{i=1}^m p_i \ln\left(\frac{\exp\left\{\frac{\beta E_i}{k_B}\right\}}{Q}\right) \\ &= -k_B \sum_{i=1}^m p_i \left(\frac{\beta E_i}{k_B} - \ln Q\right) \\ &= -\beta \sum_{i=1}^m E_i p_i + k_B \ln Q \sum_{i=1}^m p_i \\ &= -\beta U + k_B \ln Q\end{aligned}\tag{7.3.4}$$

Taking a brief detour back into the world of classical thermodynamics, recall that our definition for a differential amount of internal energy in a system is  $dU = TdS - PdV$  so that at a constant volume (because each replica in the ensemble has a constant volume by the definition of our system),  $(\partial U/\partial S)_V = T$ . Rearranging Equation (7.3.4) and utilizing this derivative allows us to solve for  $\beta$ :

$$\begin{aligned}S &= -\beta U + k_B \ln Q \\ U &= -\frac{S}{\beta} + k_B \ln Q \\ \left(\frac{\partial U}{\partial T}\right)_V &= T = -\frac{1}{\beta} \\ \beta &= -\frac{1}{T}\end{aligned}$$

A-ha! Now, we can write down our results for the canonical ensemble:

<sup>6</sup>We're sort of jumping the gun here since we haven't yet found  $\beta$ . Not to fear, though, we'll determine it later.

<sup>7</sup>A *Boltzmann factor* is an expression given as  $e^{-\beta E_i}$ . This is the most general expression. Particular examples include those expressions in the numerous ensembles we'll consider.

1.  $Q = \sum_{i=1}^m e^{-E_i/k_B T}$  is the *canonical partition function*.
2.  $p_i = \frac{1}{Q} e^{-E_i/k_B T}$  is the *Boltzmann factor* for that canonical ensemble.
3.  $S = \frac{U}{T} + k_B \ln Q$  is the entropy of the canonical ensemble

Let's try and manipulate our expression for entropy to... make it nicer, I suppose. Recall the Helmholtz free energy, defined as  $A = U - TS$ <sup>8</sup>. With a little bit of algebraic gymnastics we find that

$$A = -k_B T \ln Q$$

Hopefully, this is a satisfying result because it is directly analogous to our result for entropy of the microcanonical ensemble where  $S = k_B \ln \Omega$ . Also, hopefully this makes some sense because for the microcanonical ensemble, a.k.a. the *NVE* ensemble, the entropy is an indicator of spontaneity since the system is isolated. Similarly, for the canonical ensemble, or the *NVT* ensemble, the Helmholtz free energy is an indicator of spontaneity since it is a closed system.

So we've got the Helmholtz free energy, but what about an expression for the internal energy of a system? First, recall Equation (7.3.1) which gives us an expression for the internal energy in terms of some energies and probabilities. However, now we have those probabilities:

$$\begin{aligned} U &= \sum_{i=1}^m p_i E_i \\ &= \sum_{i=1}^m \left( \frac{\exp\{\frac{\beta E_i}{k_B}\}}{Q} \right) E_i \\ &= \frac{1}{Q} \sum_{i=1}^m E_i e^{-E_i/k_B T} \end{aligned}$$

Here we're gonna make the following (absolutely horrendous) substitution,

$$e^{-E_i/k_B T} = \frac{d}{d(1/T)} \left[ e^{-E_i/k_B T} \right] \left( \frac{-k_B}{E_i} \right)$$

which must be true by the chain rule. Thus,

$$\begin{aligned} U &= \frac{1}{Q} \sum_{i=1}^m E_i e^{-E_i/k_B T} \\ &= \frac{1}{Q} \sum_{i=1}^m -k_B \left( \frac{d}{d(1/T)} \left[ e^{-E_i/k_B T} \right] \right) \\ &= -\frac{k_B}{Q} \frac{d}{d(1/T)} \left( \sum_{i=1}^m e^{-E_i/k_B T} \right) \\ &= -\frac{k_B}{Q} \frac{d}{d(1/T)} (Q) \end{aligned}$$

This next substitution isn't as bad. Note that

$$\frac{d \ln Q(x)}{dx} = \frac{1}{Q} \frac{dQ(x)}{dx}$$

and since the partition function  $Q$  is a function of temperature we can rewrite our expression for the internal

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<sup>8</sup>We consider the Helmholtz free energy here because it is an indicator of spontaneity for constant volume and constant temperature systems. Wait... these are the conditions of the canonical ensemble!

energy to afford

$$\begin{aligned} U &= -\frac{k_B}{Q} \frac{d}{d(1/T)}(Q) \\ &= -k_B \frac{d \ln Q}{d(1/T)} \end{aligned}$$

I don't know what's going on with all these weird chain rule shenanigans but this is the last one we'll use to simplify the derivative. Note that

$$\frac{dy(x)}{d(1/x)} = -\frac{1}{1/x^2} \frac{dy(x)}{dx} = -x^2 \frac{dy(x)}{dx}$$

so that we can finally establish the following relationship for the internal energy of the canonical ensemble:

$$U = k_B T^2 \frac{d \ln Q}{dT} \quad (7.3.5)$$

### Magnets: A Case Study

Here we'll consider a simple, one-dimensional model of a magnet. Suppose we have a one-dimensional lattice made up of  $N$  magnetic dipoles, each of which are caused by the spin of an electron, either up (+1) or down (-1). The magnetization  $M$  of the magnet is  $M = \mu_B(N_\uparrow - N_\downarrow)$ , where  $N_\uparrow$  is the number of spins pointing up,  $N_\downarrow$  is the number of spins pointing down, and  $\mu_B$  is the Bohr magneton, the unit a magnetic dipole has.

Let's consider a small magnet such that  $N = 6$ . How many microstates does the lattice have? How many associated macrostates are there corresponding to a particular magnetization? First we'll address the number of microstates. At each point in the lattice an electron could be spinning one of two ways, either up or down. So, for 6 lattice points, there are  $2^6 = 64$  associated microstates. To connect this to the number of macrostates, notice that the arrangement of up-spins and down-spins is binomially distributed so that for a number  $k$  of up-spins in the lattice, there are  $\binom{6}{k}$  corresponding microstates with the same overall magnetization. Below is a table illustrating all of our choices for  $k$  and the corresponding macrostate (magnetization):

Number of up-spins, $k$	# Microstates $\binom{6}{k}$	Magnetization, $M$
0	1	$-6\mu_B$
1	6	$-4\mu_B$
2	15	$-2\mu_B$
3	20	$0\mu_B$
4	15	$2\mu_B$
5	6	$4\mu_B$
6	1	$6\mu_B$

Amazing! Let's complicate the situation. Suppose that we apply a magnetic field  $B$  to the lattice of charges. The interaction between the field and spins pointing in the same direction is favorable, whereas those pointing in opposite directions are unfavorable. We can model the energy,  $E$ , schematically as

$$E = -BM$$

Given an applied magnetic field of  $+B$  in the up-direction, write down an expression for the canonical partition function,  $Q$ , of the system. Okay! Luckily, most of the work has already been done. We know how many macrostates are present, the number of microstate associated to each macrostate, and even the magnetization

of each macrostate. Building the partition function becomes child's play. In fact, I'll do it with my eyes closed:

$$Q = \sum_{i=1}^6 g_i e^{-E_i/k_B T}$$

$$= e^{6\mu_B B/k_B T} + 6e^{4\mu_B B/k_B T} + 15e^{2\mu_B B/k_B T} + 20 + 15e^{-2\mu_B B/k_B T} + 6e^{-4\mu_B B/k_B T} + e^{-6\mu_B B/k_B T}$$

The general form for each term in this series is given above in the summation, but I'll reiterate it here. For a particular macrostate, its contribution to the partition function takes the form

$$\binom{6}{k} e^{-(BM_k)/k_B T}$$

where  $k$  is the number of up-spins in the lattice, and  $M_k$  is the associated magnetism with  $k$  up-spins. Like I said before, we computed all of these values previously. Although our expansion for  $Q$  is technically correct, oftentimes we define the ground state energy of the lattice to be zero such that  $Q$  can be rewritten as

$$Q = 1 + 6e^{2\mu_B B/k_B T} + 15e^{4\mu_B B/k_B T} + 20e^{6\mu_B B/k_B T} + 15e^{8\mu_B B/k_B T} + 6e^{10\mu_B B/k_B T} + e^{12\mu_B B/k_B T}$$

where  $k = 6$  up-spins is chosen to be the ground state energy since there are only favorable interactions.

With the partition function, write down an expression for the probability that the magnet will be in its ground state with an applied magnetic field,  $+B$ . Above we just defined the ground state to be when  $k = 6$  is the number of up-spins. Then, the probability of being in the ground state becomes

$$P(\text{ground state}) = \frac{1}{Q}$$

with  $Q$  acting as the partition function.

Now, sketch a plot of magnetization of the system as a function of temperature. COME BACK TO PLOT THIS IN PYTHON

Suppose we wish to generalize our one-dimensional model to including  $N$  magnetic dipoles, where  $N$  is some large number. If the magnet has a total magnetization  $M$ , how many microstates are there for the magnet to exist in? Express this number in terms of the known quantities,  $N$ ,  $M$ , and  $\mu_B$ . Initially, one might think that the number of microstates is given by  $W = 2^N$ , at least that's what I thought initially. However, note that we're being asked about some *fixed magnetization* so that we only care about a subset of the  $2^N$  microstates with a particular magnetization  $M$ . This magnetization will depend on the arrangement of up-spins and down-spins in the lattice, given by the multinomial coefficient,

$$W = \binom{N}{N_\uparrow N_\downarrow} = \frac{N!}{N_\uparrow! N_\downarrow!}$$

The challenge then becomes expressing the number of up-spins and down-spins in terms of the observables. To do this, first notice that it's required that  $N = N_\uparrow + N_\downarrow$ . Moreover, keep in mind that we're given

$$M = \mu_B(N_\uparrow - N_\downarrow)$$

which allows us to substitute for either of  $N_\uparrow$  or  $N_\downarrow$  into the expression for the total number of dipoles. Doing

this for  $N_{\uparrow}$ ,

$$\begin{aligned}
 N &= N_{\uparrow} + N_{\downarrow} \\
 &= \left( \frac{M}{\mu_B} + N_{\downarrow} \right) + N_{\downarrow} \\
 N - \frac{M}{\mu_B} &= 2N_{\downarrow} \\
 N_{\downarrow} &= \frac{N}{2} - \frac{M}{2\mu_B}
 \end{aligned}$$

Similarly, we can show that

$$N_{\uparrow} = \frac{N}{2} + \frac{M}{2\mu_B}$$

so that our final expression for the number of microstates in this lattice becomes

$$W = \frac{N!}{N_{\uparrow}!N_{\downarrow}!} = \frac{N!}{\left(\frac{N}{2} + \frac{M}{2\mu_B}\right)! \left(\frac{N}{2} - \frac{M}{2\mu_B}\right)!}$$

An important feature of magnets we've ignored until this point is that spins interact with their nearest neighbor as well as any applied magnetic field. When two adjacent spins point in the same direction, a favorable interaction is formed and contributes  $-J$  to the overall energy of the microstate. Similarly, when adjacent spins point in opposite directions, an unfavorable interaction occurs which contributes  $+J$  to the energy of the microstate. Consider a system of  $N = 3$  dipoles and write down an expression for the canonical partition function in the absence of a magnetic field. To do this, notice that *the only energy being contributed to the microstate is coming from nearest neighbor interactions*. So, all we need to determine is the energy coupling of each microstate. Since 3 is a pretty small number, we can just draw each microstate out and determine the coupling energy associated with each:

Microstate	$\uparrow\uparrow\uparrow$	$\downarrow\uparrow\uparrow$	$\uparrow\downarrow\uparrow$	$\uparrow\uparrow\downarrow$	$\downarrow\downarrow\uparrow$	$\downarrow\uparrow\downarrow$	$\uparrow\downarrow\downarrow$	$\downarrow\downarrow\downarrow$
Energy	$-2J$	$0$	$+2J$	$0$	$0$	$+2J$	$0$	$-2J$

Thus, our partition function can be expressed as

$$Q = 2e^{-2J/k_B T} + 4 + 2e^{2J/k_B T}$$

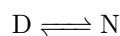
which can be rewritten by taking the ground state to be when all three dipoles are facing in the same direction to be

$$Q = 2 + 4e^{2J/k_B T} + 2e^{4J/k_B T}$$

Lastly, a quick note on the ground state configuration of the lattice we described above with  $N = 3$ . Regardless of the presence of an external magnetic field, we would expect the ground state configuration of the material to be where all of the dipoles are pointing in the same direction due to favorable nearest-neighbor interactions. In the absence of a magnetic field, this direction is effectively chosen at random. In contrast, when an external magnetic field is present we'd expect the lattice to point in the same direction as the magnetic field because this would minimize the energy of the system. Either way, energy is minimized (and the ground state is achieved) when all dipoles are pointing in the same direction.

### Two-State Systems: A Case Study

Two-state systems can be described by the equilibrium





where N is the native state and D is the denatured state. Suppose that we have a two-state system in which the energy difference between the states is  $h\nu$ . Write down a partition function for a single molecule of this type and calculate its internal energy. Using the general form for the canonical partition function and also allowing  $\Delta E = h\nu$  in this case, we have

$$\begin{aligned} Q &= g_1 e^{-E_1/k_B T} + g_2 e^{-E_2/k_B T} \\ &= 1 + e^{-h\nu/k_B T} \end{aligned}$$

as the canonical partition function for this system. Above I allowed  $g_1$  and  $g_2$  to represent the multiplicities of each state, the native and denatured forms of the molecule. However, there is no preference associated with either state (or just none that we are given) so that  $g_1 = g_2 = 1$ . Moreover, I allowed  $E_1 = 0$  to represent the ground state of the system and  $E_2 = \Delta E = h\nu$  to be the energy difference between the denatured and native states. To calculate the internal energy of the system, recall Equation (7.3.5) which gives us the internal energy in terms of the partition function. Then,

$$\begin{aligned} U &= k_B T^2 \frac{d \ln Q}{dT} = k_B T^2 \frac{d}{dT} \left[ \ln \left( 1 + e^{-h\nu/k_B T} \right) \right] \\ &= k_B T^2 \left( \frac{\frac{h\nu}{k_B T^2} e^{-h\nu/k_B T}}{1 + e^{-h\nu/k_B T}} \right) \\ &= \frac{h\nu e^{-h\nu/k_B T}}{1 + e^{-h\nu/k_B T}} \end{aligned}$$

This is the internal energy of the system. With this expression, compute the heat capacity at a constant volume for this molecule. Recall Equation (3.2.2) which relates the internal energy to the heat capacity at a constant volume. Then, the calculation is trivial:

$$\begin{aligned} C_V &= \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial}{\partial T} \left[ \frac{h\nu e^{-h\nu/k_B T}}{1 + e^{-h\nu/k_B T}} \right] \right)_V \\ &= \frac{(1 + e^{-h\nu/k_B T}) \left( \frac{h^2 \nu^2}{k_B T^2} e^{-h\nu/k_B T} \right) - (h\nu e^{-h\nu/k_B T}) \left( \frac{h\nu}{k_B T^2} e^{-h\nu/k_B T} \right)}{(1 + e^{-h\nu/k_B T})^2} \\ &= \frac{\frac{h^2 \nu^2}{k_B T^2} e^{-h\nu/k_B T} + \frac{h^2 \nu^2}{k_B T^2} e^{-2h\nu/k_B T} - \left( \frac{h^2 \nu^2}{k_B T^2} e^{-2h\nu/k_B T} \right)}{(1 + e^{-h\nu/k_B T})^2} \\ &= \frac{h^2 \nu^2 e^{-h\nu/k_B T}}{k_B T^2 (1 + e^{-h\nu/k_B T})^2} \end{aligned}$$

This is the constant-volume heat capacity of the molecule.

Let's now consider two *different* types of two-state systems that operate on very different energy levels. Suppose that the first system is the electronic absorption between a singlet ground state to a singlet excited state in which the states differ by the energy of a green photon with  $\lambda = 500$  nm. Additionally, suppose that we consider another system which represents the spin of an  $^1\text{H}$  nucleus in the presence of a 7 T magnetic field<sup>9</sup> with a resonant frequency of 300 MHz. In either case, the probability of occupying the ground state, where  $E_{gs} = 0$ , is given by

$$P(\text{ground state}) = \frac{1}{1 + e^{E_{gs}/k_B T}}$$

where  $E_{gs}$  is to be determined with the given information. Firstly, for the ground state and excited state separated by a green photon, we have that the energy difference is given by

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J/s})(2.998 \times 10^8 \text{ m/s})}{500 \times 10^{-9} \text{ m}} = 3.97 \times 10^{-19} \text{ J}$$

<sup>9</sup>The SI units of a magnetic field are “teslas,” denoted by T.

and therefore the probability of being in the ground state is given by

$$P(\text{ground state}) = \frac{1}{1 + e^{-h\nu/k_B T}} = \frac{1}{1 + 1.15 \times 10^{-42}} = 1$$

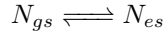
Now, for the system representing the spin of a hydrogen nucleus we have the energy difference between the ground state and excited state is given by

$$E = h\nu = (6.626 \times 10^{-34} \text{ J/s})(300 \times 10^6 \text{ s}^{-1}) = 1.99 \times 10^{-25} \text{ J}$$

so that the probability of being in the ground state becomes

$$P(\text{ground state}) = \frac{1}{1 + e^{-h\nu/k_B T}} = \frac{1}{1 + 1} = \frac{1}{2}$$

Now we consider an ensemble of  $N$  such two-state molecules. The rate constant for molecules to get excited is  $k_{gs \rightarrow es} = I(\nu)B_{12}$  where  $I(\nu)$  is the intensity of incident light at the resonant frequency and  $B_{12}$  is the “Einstein absorption coefficient.” Moreover, the rate constant for molecules to relax is  $k_{eq \rightarrow gs} = A_{21}$  where  $A_{21}$  is the “Einstein coefficient for spontaneous emission.” In a *photostationary state*, the system reaches an equilibrium where the number of molecules in the ground state becomes constant. At the photostationary state, derive an expression for the equilibrium constant  $K = A_{21}/B_{12}$ . We’ll start by expressing this two-state system with a reaction scheme:



where *gs* and *es* represent the ground state and excited state. Then, the rates of formation are given by,

$$\begin{aligned} \frac{dN_{gs}}{dt} &= -I(\nu)B_{12}N_{gs} + A_{21}N_{es} \\ \frac{dN_{es}}{dt} &= -\frac{dN_{gs}}{dt} = I(\nu)B_{12}N_{gs} - A_{21}N_{es} \end{aligned}$$

At the photostationary state, the rates of formation are zero so that we’re left with the relationship

$$\begin{aligned} \frac{dN_{es}}{dt} = 0 &= -I(\nu)B_{12}N_{gs} + A_{21}N_{es} \\ I(\nu)B_{12}N_{gs} &= A_{21}N_{es} \\ \frac{A_{21}}{B_{12}} &= I(\nu) \left( \frac{N_{gs}}{N_{es}} \right) \end{aligned}$$

Notice that  $N_{gs}$  and  $N_{es}$  are the proportion of the total number of molecules,  $N$ , which are in the ground states and excited states, respectively. So, we can rewrite the expression above as

$$\begin{aligned} \frac{A_{21}}{B_{12}} &= I(\nu) \left( \frac{N \frac{1}{1 + e^{-h\nu/k_B T}}}{N \frac{e^{-h\nu/k_B T}}{1 + e^{-h\nu/k_B T}}} \right) \\ &= I(\nu)e^{h\nu/k_B T} \end{aligned}$$

which is the “equilibrium constant” for the photostationary state.

## 7.4 The Isothermal-Isobaric (NPT) Ensemble

## 7.5 The Grand Canonical Ensemble

## 7.6 Molecular Ensembles

Our discussion on energy levels makes the canonical ensemble relatively simple to write down for *discrete* systems, that is, systems in which particles can occupy a countable number of states<sup>10</sup>. How might we model continuous systems, such as those for an ideal gas? In Section ?? we derived some key facts about the microcanonical ensemble for the continuous case of an ideal gas; here we'll try to do the same for the canonical ensemble.

Recall that our partition function for the canonical ensemble as its discretized was derived as

$$Q(N, V, T) = \sum_{i=1}^N e^{-E_i/k_B T}$$

for a system of  $N$  particles. The corresponding expression in the continuous case will be expressed as an integral:

$$Q(N, V, T) = \int e^{-\mathcal{H}/k_B T} d\vec{x}_1 \dots d\vec{x}_N d\vec{p}_1 \dots d\vec{p}_N \quad (7.6.1)$$

where  $d\vec{x}_i = dx_i dy_i dz_i$  and  $d\vec{p}_i = dp_{x_i} dp_{y_i} dp_{z_i}$  are the differential coordinates and momenta of the particle respectively, and  $\mathcal{H}$  is the *Hamiltonian*<sup>11</sup>. Already we can see how deriving an expression for the partition function in the continuous case will be more difficult: Notice that Equation (7.6.1) *has units*, in particular, it has units of *action*<sup>3N</sup>, given by (position×momentum)<sup>3N</sup>. In other words, each of the differential terms  $dx_i$  and  $dp_i$  contributes a unit of action to the expression and we have  $3N$  of those terms in total, hence the power of  $3N$ . Although we've already noticed an issue, using the canonical ensemble to derive results about an ideal gas will be exceedingly easier than using the microcanonical ensemble.

We'll start by rewriting Equation (7.6.1):

$$\begin{aligned} Q(N, V, T) &= \int e^{-\mathcal{H}/k_B T} d\vec{x}_1 \dots d\vec{x}_N d\vec{p}_1 \dots d\vec{p}_N \\ &= \int e^{-(KE+PE)/k_B T} d\vec{x}_1 \dots d\vec{x}_N d\vec{p}_1 \dots d\vec{p}_N \\ &= \int e^{-PE/k_B T} d\vec{x}_1 \dots d\vec{x}_N \int e^{-\left(\sum_{i=1}^N \frac{m \vec{v}_i^2}{2k_B T}\right)} d\vec{p}_1 \dots d\vec{p}_N \\ &= \int (1) dV_1 \dots dV_N \int e^{-\left(\sum_{i=1}^N \frac{\vec{p}_i^2}{2mk_B T}\right)} d\vec{p}_1 \dots d\vec{p}_N \\ &= V^N \int e^{-\left(\sum_{i=1}^N \frac{\vec{p}_i^2}{2mk_B T}\right)} d\vec{p}_1 \dots d\vec{p}_N \end{aligned} \quad (7.6.2)$$

In line 4 we substituted  $dx_1 dy_1 dz_1 = dV$  for all  $N$  triples in the integral for the potential energy, affording  $V^N$ . Additionally, we expressed the kinetic energy in terms of momenta instead of velocity. To see why, we'll manipulate the kinetic energy integral below:

$$\begin{aligned} \int e^{-\left(\sum_{i=1}^N \frac{\vec{p}_i^2}{2mk_B T}\right)} d\vec{p}_1 \dots d\vec{p}_N &= \int e^{-\left(\frac{\vec{p}_1^2 + \vec{p}_1^2 + \dots + \vec{p}_N^2}{2mk_B T}\right)} d\vec{p}_1 \dots d\vec{p}_N \\ &= \int e^{-\left(\frac{\vec{p}_1^2}{2mk_B T}\right)} d\vec{p}_1 \int e^{-\left(\frac{\vec{p}_2^2}{2mk_B T}\right)} d\vec{p}_2 \dots \int e^{-\left(\frac{\vec{p}_N^2}{2mk_B T}\right)} d\vec{p}_N \end{aligned}$$

<sup>10</sup>The number of states may be countably *infinite*, yet countable nonetheless.

<sup>11</sup>The *Hamiltonian* is an operator which corresponds to the total energy of a system, including both the kinetic and potential energy. This operator comes up much more often in quantum mechanics where I'll provide a larger discussion on it. For now, however, we'll use it to represent the total energy of a system.

In the last line we have a succession of Gaussian integrals, each of which has a mean of zero and variance  $mk_B T$ . Furthermore, they're unnormalized so that they'll evaluate to the normalization factor. Continuing with integration,

$$\begin{aligned} \int e^{-\left(\frac{\vec{p}_1^2}{2mk_B T}\right)} d\vec{p}_1 \int e^{-\left(\frac{\vec{p}_2^2}{2mk_B T}\right)} d\vec{p}_2 \cdots \int e^{-\left(\frac{\vec{p}_N^2}{2mk_B T}\right)} d\vec{p}_N &= \sqrt{2\pi mk_B T} \sqrt{2\pi mk_B T} \cdots \sqrt{2\pi mk_B T} \\ &= (2\pi mk_B T)^{3N/2} \end{aligned}$$

Thus, our partition function for the canonical ensemble of an ideal gas is given by

$$Q = V^N (2\pi mk_B T)^{3N/2}$$

But Sam! You forgot about the issue that this partition function has units! That is an excellent point. So, how might we remedy this?

Well, we need a quantity with units of action, preferably one that can be expressed as position times momentum. This quantity is given exactly by the *Heisenberg uncertainty principle*, which asserts that  $\Delta x \Delta p \propto h$ , that is, the product of the uncertainty in the position and momentum of a particle is directly proportional to Planck's constant. So, dividing our expression by  $h^{3N}$  will afford a dimensionless number. Hence, our partition function for the molecular ensemble is

$$Q = \frac{V^N (2\pi mk_B T)^{3N/2}}{h^{3N}} \quad (7.6.3)$$

Interestingly, if you consider the quantity  $\sqrt{2\pi mk_B T}/h$ , you'll notice that it has units of  $(\text{length})^{-1}$ , encouraging us to rewrite the partition function in a new way, using a *wavelength*  $\lambda$ ,

$$Q = \left( \frac{V}{\lambda^3} \right)^N \quad (7.6.4)$$

where  $\lambda = h/\sqrt{2\pi mk_B T}$  is the *De Broglie* or *thermal wavelength*, and it expresses how much “space” a particle of an ideal gas occupies.

The other problem associated with our partition function is more subtle than the last, however, it will become more clear when we consider the entropy of the ensemble. Recall from Section ?? our expression for the entropy of a particle within the canonical ensemble:

$$\begin{aligned} S &= \frac{U}{T} + k_B \ln Q \\ &= \end{aligned}$$

### 7.6.1 Molecular Ensembles in Two Dimensions

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## 7.7 The Maxwell-Boltzmann Distribution

The *Maxwell-Boltzmann distribution* is a probability distribution that gives the provides the probability of finding a particle at some speed as a function of temperature. The density function for this distribution is,

$$f(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{1}{2} \left( \frac{mv^2}{k_B T} \right)}, \quad -\infty < v < \infty \quad (7.7.1)$$

## 7.8 Information Theory Applied to Statistical Mechanics

*Information theory* is the study of data quantification, storage, and communication, and is at the intersection of myriad scientific fields, one of which is statistical mechanics. The key measure of information theory is *Shannon entropy*<sup>12</sup> which quantifies the amount of uncertainty involved in the outcome of some process. For example, there is more entropy associated with rolling a fair, 6-sided die than there is tossing a fair coin since there are more possible outcomes for rolling the die. Additionally, we might also say that the outcome of rolling the die offers more *information* about the system since there is more entropy associated with each outcome.

The idea of “information content” in an outcome is one of the core ideas of Shannon entropy. To restate in more general terms what I said above, if we are observing a process and a highly likely event occurs, the outcome carries very little information. Inversely, if a very unlikely event occurs, the outcome is much more informative. Claude Shannon (the same guy who “Shannon entropy” is named after) posited that the information of an event must meet a specific set of axioms, all of which are satisfied by defining the information content as

$$I(x) = -\log_2(p_x) \quad (7.8.1)$$

where  $p_x$  is the probability of event  $x$  occurring.<sup>13</sup>

Insofar as we’ve discussed entropy it’s been constrained to the context of thermodynamics which, while that’s good considering this is a thermodynamics class, after all, doesn’t offer other, possibly more helpful, ways of building an intuition behind what the entropy of a system characterizes. To provide a complete connection from information theory and some computer science to thermodynamics, we’ll motivate our discussion by asking the simple question: what exactly causes our computers to heat up?

### 7.8.1 Entropy as Uncertainty

Within the study of information theory, the *Shannon entropy* of an outcome is defined as the expectation of the information, written

$$H(x) = \langle I(x) \rangle = -\sum_{i=1}^N p_i \log_2(p_i) \quad (7.8.2)$$

where the outcome  $x$  consists of  $N$  particles. To quickly provide some intuition behind how we could use this formula, consider the entropy of the alphabet. Suppose that we choose letters at random. Assuming that each letter of the alphabet has an equal probability of being chosen, the entropy is given by

$$H_{\text{alphabet}} = -\sum_{i=1}^{26} \frac{1}{26} \log_2\left(\frac{1}{26}\right) = \log_2 26 \approx 4.7 \quad (7.8.3)$$

Interestingly, and potentially obviously depending on how much one has paid attention during lecture, the Shannon entropy of a particular outcome *is exactly the same as the Gibbs entropy* (up to a constant), which is derived directly from the Boltzmann equation,  $S = k_B \ln W$ . Note that,

$$S = k_B \ln W = -k_B \sum_{i=1}^N p_i \ln p_i = -k_B \ln 2 \sum_{i=1}^N p_i \left( \frac{\ln p_i}{\ln 2} \right) = -k_B \ln 2 \sum_{i=1}^N p_i \log_2 p_i = (k_B \ln 2) H \quad (7.8.4)$$

Let us suppose we didn’t recognize this equivalence and instead used the Shannon entropy to determine the values of the  $p_i$  which will maximize the entropy. As we saw with the definition of information content in Equation (7.8.1), the information is monotonically decreasing as the probability of any one outcome decreases.

<sup>12</sup>I’ll try my best to distinguish between Shannon entropy and thermodynamic entropy throughout this section but you’ll probably just have to figure out which one I’m talking about based on context clues. I believe in you!

<sup>13</sup>The choice of base for the logarithm is arbitrary and will only effect the units in the end. The most common choice is base 2 which affords units of “bits”. Another common choice is to use the natural base  $e$ , affording units of “nats”.

In other words, the Shannon entropy for a probability distribution will increase as the probability of any outcome from the distribution decreases. Conveniently, the postulate of *a priori* equal probabilities with  $p_i = \frac{1}{\Omega}$  where  $\Omega$  is the sample space, satisfies this property. Then, the Shannon entropy is given by

$$\begin{aligned} H &= - \sum_{i=1}^{\Omega} \frac{1}{\Omega} \log_2 \frac{1}{\Omega} \\ \left( \frac{1}{k_B \ln 2} \right) S &= \log_2 \Omega \\ S &= k_B \ln \Omega \end{aligned} \tag{7.8.5}$$

which agrees exactly with the Boltzmann equation.

The equivalence illustrated in Equations (7.8.4) and (7.8.5) prompts us to rethink (if not already having thought) of *entropy as uncertainty*. For example, suppose we are interested in a gas contained within a box. All of the particles have some well-defined position and momentum and if we knew all of these position and momenta there would only be one microstate possible for the gas and therefore zero entropy. Clearly, though, the entropy of a gas is nonzero. It's nonzero exactly because we don't know the positions and momenta of the particles. Hence, entropy is not necessarily a property of the gas but instead a property of our knowledge of the gas.

### 7.8.2 The Irreversibility of Information Storage

In the preceding section we made an informal connection between thermodynamic entropy and Shannon entropy, relying on an observation as opposed to a rigorous derivation. This connection, however, can not only be shown rigorously but also proven to be an equivalence. That is, showing that thermodynamic entropy and Shannon entropy are exactly the same. This result will require slightly more work...

Recall the question that sparked our discussion regarding computers and their tendency to heat up as we use them. Clearly, some energy is being dissipated by our machines during this process. In 1961, the physicist Rolf Landauer was interested in minimizing this energy loss and considered the existence of a computer which could operate with no loss of energy. He considered a model of a bit<sup>14</sup> with a double-well, illustrated in Figure 7.1. The first question Landauer posited was whether or not we could switch the sign of the bit from 0 to 1 without expending any energy.

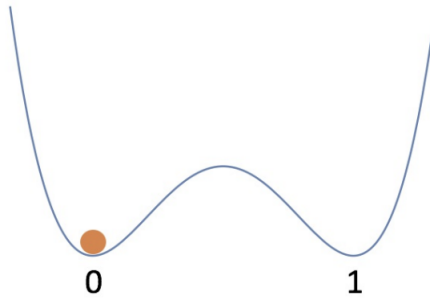


Figure 7.1: Double well model of bit storage.

Seemingly, the answer is yes. Following the scheme in Figure 7.2, attaching a counterweight to the ball representing our bit and giving an infinitesimal nudge to the counterweight will allow us to switch the sign of the bit. Another infinitesimal nudge to stop the counterweight stops the ball, affording a reversible reaction without the expenditure of energy.<sup>15</sup>

<sup>14</sup>A “bit” is the unit of storage for a system using binary. That is, a binary integer represented by either 0 or 1 requires 1 bit of

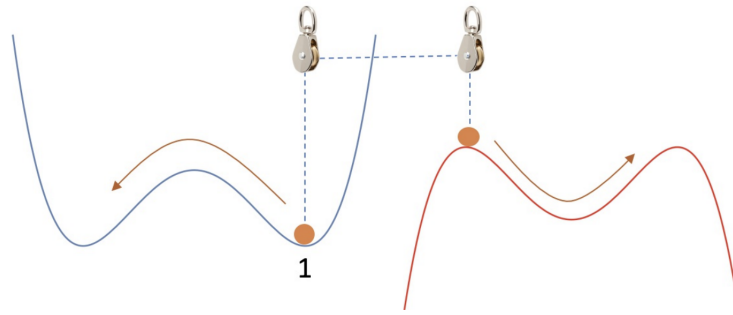


Figure 7.2: Double well model of bit storage using pulleys to avoid expending energy to switch the sign of a bit.

At this point we need to address the issue of knowing the initial state of the bit. Above, we naively assumed that every time we go to switch the sign of the bit we “guess” correctly, in that we don’t try and switch the state of a 0 bit to 0. So, can our pulley system address the issue of not knowing the initial state of the bit? The answer is no.

In particular, the answer is no for any sort of over-engineered apparatus you can think of. The reason is that we are using Newton’s Laws to switch the sign of the bit (the infinitesimal nudge). Recall that Newton’s Laws are time-invariant so that anything we do in the forward direction of time must be equally possible and well-defined in the reverse direction of time. Swapping a 1 to a 0 corresponds to swapping a 0 to a 1 in the reverse direction. So, a function or process which can simultaneously swap a 1 and a 0 to a 0 is clearly not invertible. If the final state of the system is a 0 how can we be sure of the initial state (assuming that we’ve created the machine I’ve already said was impossible to create)?<sup>16</sup>

The calculation described above, swapping a bit regardless of whether it is a 1 or a 0 to a 0, is performed all the time by computers. How? Well, the process is fairly straightforward *if we’re allowed to dissipate energy*. For example, if there is friction in our double-well model, the process could involve smacking a mallet on the “1” side with enough energy to knock the bit down the well and over the adjacent hill. If there is no bit present on the 1 side, the 0 remains a 0. If there is a bit present, the 1 rolls up the hill and is slowed by friction, ultimately resting in the well corresponding to 0. Note that this wouldn’t work if friction we’re not present since the ball would have enough energy to roll back up the hill and arrive in the “1” well again. To address the question of how realistic a system like this is, suppose that the ball representing our bit is stored in the spin of a magnet on some magnetic tape. The mallet, then, may be an external magnetic field. No matter how you imagine our information to be stored, we arrive at the conclusion that *erasing energy requires energy to be dissipated as heat*, also known as *Landauer’s principle*.

Erasing information is an essential step in computation; every time information is stored the corresponding information which existed there previously is erased. Take, for example, what I’m writing now. “ ” contains some information, it’s meaningless, but it’s something. “1” now it contains new information, potentially more meaningful to you and I. In any case, the information stored in the empty space was erased upon the addition of the 1.

The key element to showing that the erasure of information is impossible without the loss of energy was the reversibility of the laws of physics. Thus, thermodynamic entropy increases when information is discarded. The connection between thermodynamic entropy and information entropy has been pushed further by scientists asking question such as, “what is the minimum amount of energy required to perform a computation?” More generally, what are the limits of computing? This is getting more into the realm of computer science than I

storage.

<sup>15</sup>If I may interject to comment on the setup of our apparatus. Clearly, using counterweights and pulleys to store information in a computer is unrealistic. This, however, is a thought experiment and so the plausibility of our setup is of no concern. That’s an issue for the engineers.

<sup>16</sup>More technically you might say that we require an invertible function which is also *not* injective. Even writing this down makes me fear the NSA is listening and is going to have me off’d. A function is invertible *if and only if* it is injective. So, the required function to make our imaginary apparatus work is nonsense!

care for, so those answers will be relegated to another time.

### 7.8.3 Maxwell's Demon

With our newly established expertise in information theory we can tackle one of the most famous and vexing paradoxes regarding entropy, invented by James Maxwell in 1867. As originally postulated, the paradox is stated as follows:

*... if we conceive of a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are as essentially finite as our own, would be able to do what is impossible to us. For we have seen that molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions,  $A$  and  $B$ , by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from  $A$  to  $B$ , and only the slower molecules to pass from  $B$  to  $A$ . He will thus, without expenditure of work, raise the temperature of  $B$  and lower that of  $A$ , in contradiction to the second law of thermodynamics.*

In layman's terms, we can imagine a container of gas with a partition in the middle separating sides  $A$  and  $B$ , each of which have an equal amount of energy contained within them on average. A "demon" observes the molecules on both sides and allows molecules with an above average-velocity to pass into side  $A$  while only allowing the below average-velocity particles to stay on side  $B$ , all while dissipating very little energy compared to that gained by the system upon establishing an energy gradient. Thus, we're left with a box that has an energy gradient between the two sides, with  $A$  having particles with an average energy greater than that of the average energy of the particles on side  $B$ . Since the box started with a uniform energy across the partition separating sides  $A$  and  $B$  we've seemingly violated the second law of thermodynamics.

To prove that this situation does not in fact violate the second law of thermodynamics we'll invoke Landauer's principle. In order for the demon to allow the molecule to pass through the partition it must first acquire some information about the particle, whether it be the speed, momentum, or energy. Then, to accurately judge which side the *next* particle should belong to the demon must erase the information previously stored about the speed, momentum, or energy to make space for the corresponding information of the new particle. Discarding the previously held information immediately causes an increase in entropy, as we've seen. Moreover, the demon cannot store any information indefinitely, implying that the storage of *any* information regarding the system of gas particles ultimately causes an increase in entropy.<sup>17</sup>

This thought experiment clarifies why information entropy is equivalent to thermodynamic entropy. Suppose that the demon described above also kept a finite tape of 0's in his back pocket. For every bit of information he gathers about a particle approaching the partition, he may record the info on the tape with either a 1 or a 0 (recall that we're assuming the information he gathered regarding the particles can be represented in binary). Then, we must include the tape in our definition of the system. In doing so, the entropy of the gas may very well decrease as he selects for which particles enter side  $A$  and which enter side  $B$ , however, the entropy of the *system* never decreases because the information stored in the particles isn't lost but instead transferred to the tape.

In this way, Maxwell's demon was resolved after over 100 years of turmoil. In his lectures on computation Feynman comments on Landauer's principle:

This realization that it is the erasure of information, and not measurement, that is the source of entropy generation in the computational process, was a major breakthrough in the study of reversible computation.

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<sup>17</sup>This was illustrated by Charles Bennett in a paper titled "The Thermodynamics of Computation — a Review," published in 1982.



## CHAPTER

# 8

# HELIX-COIL THEORY

*Helix Coil Theory*

- David Goodstein

The *helix-coil transition model* is a formalized application of the partition functions developed in statistical mechanics to help analyze the multistate conformational transitions of linear polymers. In particular, we'll be considering the formation of an  $\alpha$ -helix from a polypeptide chain.

You're probably already familiar with  $\alpha$ -helices as they are among the most common types of protein secondary structure.<sup>1</sup> The reason these structures are so common is due to the natural stability and optimality of the intermolecular interactions and bond lengths. Some common examples are  $\alpha$  keratin, a principle component of the epidermis and related appendages such as hair and nails, as well as collagen, which bears strong, insoluble fibers responsible for connective tissue.

As a motivating example, consider a polypeptide of length 5, that is, one composed of 5 amino acid residues. We can model the partitioning of energy states using the canonical ensemble. Although using the NPT ensemble would be better suited to this situation, we'll stick with the canonical ensemble for convenience. An important aspect of our model to keep in mind is that *entropy is inherently represented*. That is, microstates which are energetically favored are necessarily entropically favored. For our case of 5 residues... ya know I was about to try and make a table but then I thought better of it. There's a representation of all 32 microstates in the lecture slides or either of the two textbooks for this class just go look at those.

The favorable macrostates are so because they have a greater *degeneracy*, that is, they are represented more. Hence, we can rewrite our canonical partition function as

$$Q = \sum_{i=1}^{m=2^N} \lambda_i e^{-\frac{E_i}{RT}} \quad (8.0.1)$$

where  $\lambda_i$  represents the frequency of the microstate and  $m = 2^N$  is the total number of microstates for  $N$  amino acid residues. For example, in the case of one helical residue among four other coils, there are  $\binom{5}{1} = 5$  degenerate states and therefore  $\lambda_1 = 5$ . Experiments can't observe the populations of 32 unique microstates,

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<sup>1</sup> Alongside  $\beta$ -sheets.

hence, we define the *fractional helicity* as

$$\langle f_H \rangle = \sum_{i=1}^m p_i f_{H,i} = \frac{1}{Q} \sum_{i=1}^m f_{H,i} e^{-\frac{E_i}{RT}} \quad (8.0.2)$$

Since  $f_H$  is defined as the *average number of helical residues divided by the length of the peptide*, we can express the expression above alternatively,

$$\langle f_H \rangle = \frac{\langle j \rangle}{N} = \frac{1}{N} \sum_{j=1}^N j \times p_j \quad (8.0.3)$$

where  $j$  is the average helicity of the macrostate<sup>2</sup> Although a summation over the number of residues offers a significant simplification from a summation over the total number of microstates, our work is far from done<sup>3</sup>. In the succeeding sections we'll develop models which significantly reduce the complexity of our expressions for the partition function, affording considerable insight into key aspects of helix-coil energetics.

P.S. I used  $Q$  to express the partition function in the case of every model, so depending on the context  $Q$  will take on a different expression. I don't think this will cause any confusion, but just in case it does, try and use context clues I guess.

### 8.0.1 The Noncooperative Model

The simplest model for helix formation we'll consider is *noncooperative formation* in which each residue can be thought of as being "independent" of its neighbor. That is, the existence of a helical coil in the polymer does not influence the formation of helical coils in adjacent residues.

This assumption allows us to use a single expression for the free energy associated with the helical transition. That is, if the change in free energy associated with one helical residue is given by  $\Delta\tilde{G}_{c \rightarrow h}^\circ$ , then the change in free energy for the same transition across five residues is  $5\Delta\tilde{G}_{c \rightarrow h}^\circ$ . To simplify this expression we can define a new variable representing the free energy conversion for a single residue as

$$\kappa = e^{-\Delta\tilde{G}_{c \rightarrow h}^\circ/RT} \quad (8.0.4)$$

$\kappa$  can be thought of as a pseudo-equilibrium constant for a single residue<sup>4</sup>. If we consider the simple example mentioned a moment ago for the difference between the transition of one residue versus five residues to the helical transition, we could express the transition energy of one residue as  $\kappa$  and the transition energy as  $\kappa^5$  (convince yourself that this is true. It isn't very hard).

With the energy associated with the coil-to-helix transition found, we can now try and discern the partition function for all possible states of a peptide within the noncooperative model. The partition function is given exactly as we're used to,

$$Q = \sum_{j=1}^N g_j e^{-\Delta\tilde{G}_j^\circ/RT}$$

which is analogous to Equation (8.0.1). Here, however, we've used  $g_j$  to represent the degeneracy of each microstate. Since the likelihood of each microstate is independent of one another (this is our primary assumption under the noncooperative model), the degeneracy factor can be represented as a binomial coefficient and the

<sup>2</sup>The switch between using  $i$  and  $j$  as our iteration variables is intentional:  $i$  is used in a summation through all *macrostates* whereas  $j$  is used in a summation through all *residues*.

<sup>3</sup>Is our work ever done? The answer is no. Always strive to be better.

<sup>4</sup>It's not quite an equilibrium constant because there is more chemistry going on after folding. Intermolecular interactions between residues on the peptide also contribute to the free energy of transition but aren't captured by  $\kappa$ .

partition function can be simplified:

$$Q = \sum_{j=1}^N \binom{N}{j} e^{-\Delta\tilde{G}_j^{\circ}/RT} = \sum_{j=1}^N \binom{N}{j} e^{-j\Delta\tilde{G}_{c\rightarrow h}^{\circ}/RT} = \sum_{j=1}^N \binom{N}{j} \kappa^j$$

$$Q = (1 + \kappa)^N \quad (8.0.5)$$

Equation (8.0.5) illustrates clearly the utility of the noncooperative model: The partition function for the peptide can be represented in a simple, concise expression. Intuitively, this result should make sense. For each residue we're effectively flipping a coin, as each one can either exist in the coiled or helical state. With  $N$  residues, then, there are  $2^N$  microstates. The partition function, however, considers *energies*, not just microstates. So, the change in free energy associated with the transition can either be 0 (where the residue exists in the coiled conformer) or  $\Delta\tilde{G}_{c\rightarrow h}^{\circ}$  (where the residue has transitioned to the helix). The Boltzmann factors come naturally from either of these two values and the partition function with those, using the same logic mentioned a moment ago.

With the partition function defined we can ascertain the fractional helicity of peptide using Equation (8.0.3):

$$\begin{aligned} \langle f \rangle &= \frac{\langle j \rangle}{N} = \frac{1}{N} \sum_{j=1}^N j p_j \\ &= \frac{1}{N} \sum_{j=1}^N j \frac{\binom{N}{j} \kappa^j}{(1 + \kappa)^N} = \frac{1}{N(1 + \kappa)^N} \sum_{j=1}^N \binom{N}{j} j \kappa^j \end{aligned}$$

Here we can take advantage of the chain rule to reexpress

$$j \kappa^j = \kappa \frac{d(\kappa^j)}{d\kappa}$$

and substitute into our expression above:

$$\begin{aligned} \frac{1}{N(1 + \kappa)^N} \sum_{j=1}^N \binom{N}{j} j \kappa^j &= \frac{1}{N(1 + \kappa)^N} \sum_{j=1}^N \binom{N}{j} \kappa \frac{d(\kappa^j)}{d\kappa} \\ &= \frac{\kappa}{N(1 + \kappa)^N} \frac{d}{d\kappa} \sum_{j=1}^N \binom{N}{j} \kappa^j \\ &= \frac{\kappa}{N(1 + \kappa)^N} \frac{d(1 + \kappa)^N}{d\kappa} \\ &= \frac{\kappa}{N(1 + \kappa)^N} \left( N(1 + \kappa)^{N-1} \right) \\ &= \frac{\kappa}{1 + \kappa} \end{aligned} \quad (8.0.6)$$

Equation (8.0.6) constitutes the fractional helicity for the noncooperative model of an  $\alpha$ -helix.

Here is a list of all the results we've derived for the noncooperative model:

$Q = (1 + \kappa)^N$  is the partition function for a polymer with  $N$  residues. Here,  $\kappa = e^{-\Delta\tilde{G}_{c\rightarrow h}^{\circ}/RT}$  is the "pseudo-equilibrium constant."

$p_i = \frac{\binom{N}{i} \kappa^i}{(1 + \kappa)^N}$  is the probability of a polymer having  $i$  helical residues under the noncooperative model.

$\langle f_H \rangle = \frac{\kappa}{1 + \kappa}$  is the fractional helicity of a polymer under the noncooperative model.

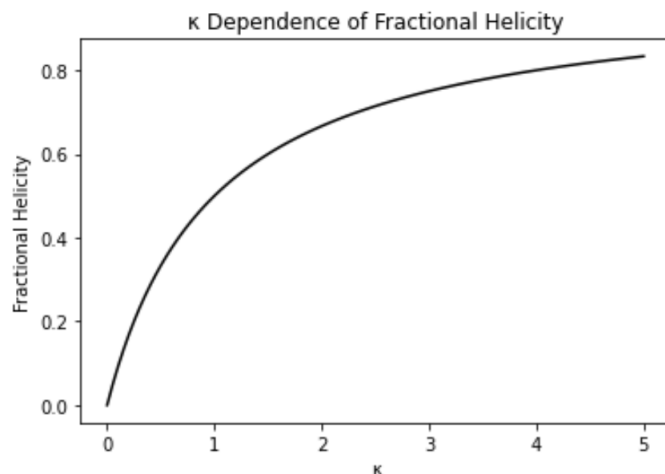


Figure 8.1: The fractional helicity of a polymer as a function of  $\kappa$  takes the shape of a *rectangular hyperbola*, indicative of a noncooperative relationship. This type of graph is in contrast to a *sigmoid* which (typically) indicates cooperativity.

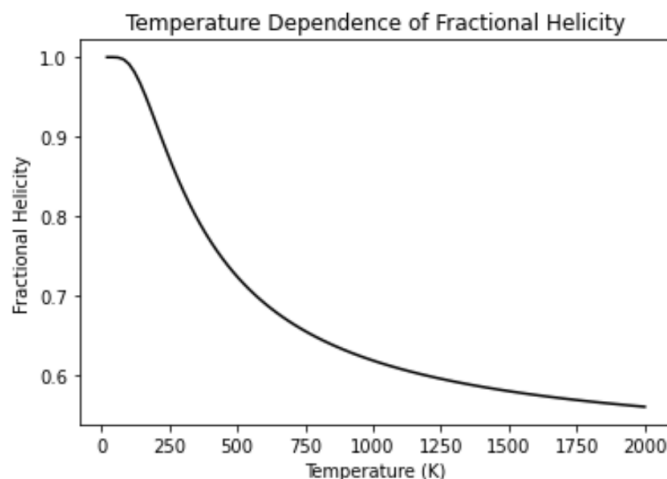


Figure 8.2: The fractional helicity of a polymer as a function of temperature follows an exponential decay. Notice, however, that this exponential decay is *very slow*. At 2000 K the peptide maintains a fractional helicity greater than 50%, even though there are barely any proteins which haven't denatured well before this temperature. This discrepancy between our intuition and our results incentives the definition of a cooperative model for  $\alpha$ -helix formation. Note that above, a value of  $\Delta\tilde{G}_{c\rightarrow h}^\circ = -4$  kJ/mol was chosen for no reason aside from that was what Dr. Fried used in the slides.

## 8.1 Cooperativity

*Cooperativity in protein folding* is the phenomenon where one part of a peptide chain folding into a tertiary structure makes it more likely that adjacent parts of the peptide do the same. The converse to this is also true: The *unfolding* of one part of a protein influences adjacent residues to do the same, hence why denaturation can happen so quickly at sufficient temperatures.

Depending on the context, cooperativity can take on slightly different meanings and is why I specified cooperativity among proteins instead of just in general. In enzymatic catalysis, for example, cooperativity can be thought of in terms of ligand binding.

The most simple model of cooperativity we could invoke for polymer folding is one where each residue may affect those that it's directly adjacent to but no others. This requires we define a *coupling strength*, oftentimes denoted  $J$ ,<sup>5</sup> and is typically negative as to be energetically favorable. Just as there is an associated Boltzmann

<sup>5</sup>You may recognize  $J$  from the splitting of peaks in NMR spectra. In the context of cooperativity, however, the term “coupling” takes on a slightly varied meaning.

constant for the change in free energy of folding,  $\kappa$ , there is one for coupling, denoted  $\tau$ :

$$\kappa = e^{-\Delta\tilde{G}_{c\rightarrow h}^{\circ}/RT}, \quad \tau = e^{-J/k_B T}$$

The Hamiltonian (recall that the Hamiltonian is an operator which represents the total energy of a system) for a polymer of  $N$  residues becomes

$$\mathcal{H} = J \sum_{i=1}^N \sigma_i \sigma_{i+1} + \Delta\tilde{G}_{c\rightarrow h}^{\circ} \sum_{i=1}^N \sigma_i, \quad \sigma_i \in \{0, 1\} \quad (8.1.1)$$

where  $\sigma_i = 1$  corresponds to the existence of a helical residue on the peptide and  $\sigma_i = 0$  a coiled residue.

### 8.1.1 The Zipper Model

The *zipper model* is a model for cooperative protein folding that assumes that once helices form, they “zip up” into a continuous block. With this simplification, the coupling constant  $\tau$  is introduced into the partition function such that the Boltzmann factor for each microstate is of the form  $\kappa^j \tau^{j-1}$ . This simplification omits the microstates which have blocks of helices separated by one or more coiled segments. As an example, for a pentapeptide the zipper model does not accurately model microstates such as *hchch* or *hchhhh*. In practice, however, this loss is negligible as long as  $\tau$  is large, normally at  $\tau = 10^3$  or greater.

The simplification in the zipper model allows us to write the partition function as a sum over all helical levels  $j$ , where  $j = 1, \dots, N$  for a peptide with  $N$  residues, using the Boltzmann factor  $\kappa^j \tau^{j-1}$  described above. With a little bit of mathematical intuition (and page 386 of Barrick) we can deduce that the number of microstates *involving helical residues* can be counted by

$$W = N - j + 1$$

Then, the partition function can be described by

$$Q = 1 + \sum_{j=1}^N W \kappa^j \tau^{j-1} = 1 + \sum_{j=1}^N (N - j + 1) \kappa^j \tau^{j-1} \quad (8.1.2)$$

where the +1 term accounts for the completely coiled peptide chain. Equation (8.1.2) is adequate for short peptide chains where the summation can be computed by hand easily. For longer chains, however, a closed form solution for the partition function would be far less computationally-intensive. With a little bit of algebraic gymnastics, beginning with bringing  $\kappa$  and  $\tau$  to the same power, this can be achieved:

$$\begin{aligned} Q &= 1 + \sum_{j=1}^N (N - j + 1) \kappa^j \tau^{j-1} \\ &= 1 + \frac{1}{\tau} \sum_{j=1}^N (N - j + 1) \kappa^j \tau^j \\ &= 1 + \frac{1}{\tau} \left[ \sum_{j=1}^N (N + 1) (\kappa \tau)^j - \sum_{j=1}^N j (\kappa \tau)^j \right] \\ &= 1 + \frac{1}{\tau} \left[ \sum_{j=1}^N (N + 1) (\kappa \tau)^j - \kappa \sum_{j=1}^N \frac{\partial}{\partial \kappa} (\kappa \tau)^j \right] \end{aligned}$$

The derivative in the last line is introduced the same way as it was in Equation (8.0.6), this time making sure to keep  $\tau$  constant. Notice that we have two summations, each of which is a *power series*. I cover the derivation

of a closed form solution to the power series in Section ?? so that we can rewrite the expression above as

$$Q = 1 + \frac{1}{\tau} \left[ (N+1) \frac{\kappa\tau[(\kappa\tau)^N - 1]}{\kappa\tau - 1} - \kappa \frac{\partial}{\partial \kappa} \left( \frac{\kappa\tau[(\kappa\tau)^N - 1]}{\kappa\tau - 1} \right) \right] \quad (8.1.3)$$

and evaluating the derivative affords the desired closed form solution for the partition function of the zipper model:

$$Q = 1 + \kappa \left[ \frac{(\kappa\tau)^{N+1} - (N+1)(\kappa\tau) + N}{(\kappa\tau - 1)^2} \right] \quad (8.1.4)$$

Using the partition function we can define the fractional helicity for a polymer under the zipper model. As before, when we did this for the noncooperative model, this can be done using the probabilities of a microstate containing  $j$  helices:

$$\langle f_H \rangle = \frac{1}{N} \sum_{j=1}^N j p_j = \frac{1}{NQ} \sum_{j=1}^N j(N-j+1) \kappa^j \tau^{j-1} \quad (8.1.5)$$

The derivation is really long and uses a lot of techniques we've already covered in finding closed form solutions to the partition functions, so I'm not gonna do it here. Ultimately, we arrive at the following closed form solution for the fractional helicity:

$$\langle f_H \rangle = \frac{2\kappa^2\tau[1 - (\kappa\tau)^N] + N\kappa[1 - \kappa\tau][1 + (\kappa\tau)^{N+1}]}{N(\kappa\tau - 1)\{1 + \kappa(N - 2\tau) + \kappa^2\tau[\tau - 1 - N + (\kappa\tau)^N]\}} \quad (8.1.6)$$

Graphing fractional helicity versus  $\kappa$  affords a sigmoid, corroborating the assumption about this model being cooperative. Another trend that appears is that *longer peptides* show sharper helical transitions as a function of  $\kappa$ . This is because longer peptides have more initiation sites and once a helix has been initiated, longer stretches of the helix can propagate and the peptide becomes helical by cooperativity.

Additionally, if we graph fractional helicity versus  $\tau$ , unsurprisingly, we find that helix formation likelihood increases as  $\tau$  increases. A rather surprising aspect of this plot, however, is that even at  $\tau = 1$  when there are no favorable or unfavorable interactions between helices,  $\alpha$ -helix formation is still largely sigmoidal whereas we would expect a rectangular hyperbola, which is the case of noncooperativity. This discrepancy arises due to the fact that the partition function omits those microstates which are helical *with gaps*. This assumption is okay when  $\tau$  is large (discussed earlier) so that “gapped” microstates have negligible populations. For small  $\tau$  values, these microstates are significantly populated, thereby changing the shape of the plot.

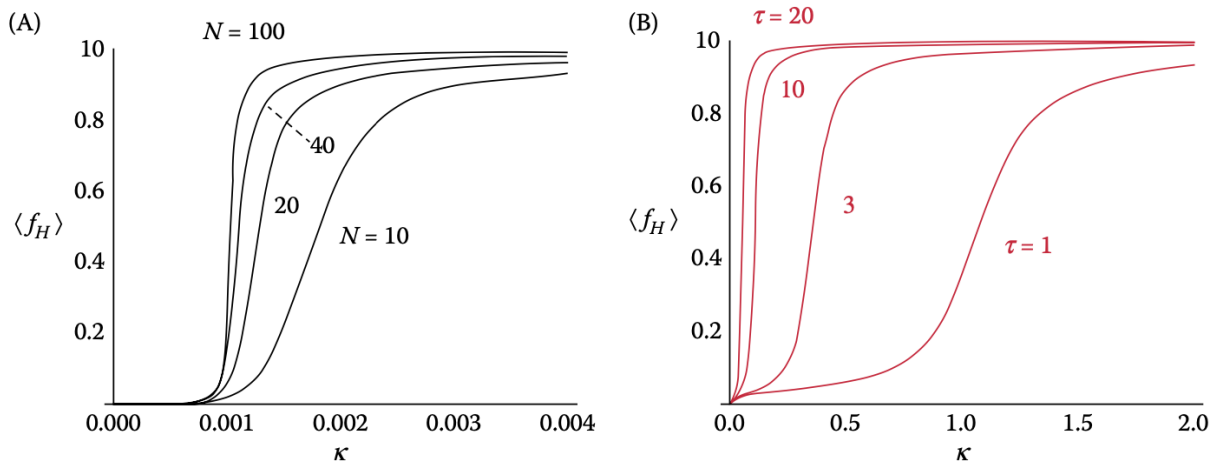


Figure 8.3: (A) The fractional helicity as a function of  $\kappa$  as the length of the polymer increases. Clearly, as  $N$  tends to infinity the affinity for a polymer to become an  $\alpha$ -helix increases. (B) The fractional helicity as a function of  $\kappa$  as the coupling constant is (modestly) increased. For  $\tau = 1$ , the unexpected shape is a result of the assumptions made under the zipper model, as discussed above. As  $\tau$  increases, the affinity for the polymer to become helical increases which agrees with our intuition.

Here is a list of all results we've derived for the zipper model for  $\alpha$ -helix formation:

$Q = 1 + \kappa \left[ \frac{(\kappa\tau)^{N+1} - (N+1)(\kappa\tau) + N}{(\kappa\tau - 1)^2} \right]$  is the partition function for the zipper model.

$p_i = \frac{(N-i+1)\kappa^i\tau^{i-1}}{Q}$  is the probability of there being  $i$  helices in a peptide of  $N$  residues.

$\langle f_H \rangle = \frac{2\kappa^2\tau[1 - (\kappa\tau)^N] + N\kappa[1 - \kappa\tau][1 + (\kappa\tau)^{N+1}]}{N(\kappa\tau - 1)\{1 + \kappa(N - 2\tau) + \kappa^2\tau[\tau - 1 - N + (\kappa\tau)^N]\}}$  is a closed-form solution to the fractional helicity of a polymer under the zipper model.

### 8.1.2 The Nearest-Neighbor Model

The *nearest-neighbor model* for  $\alpha$ -helix formation remedies the assumptions and issues made by and raised in the zipper model by utilizing a *transfer matrix*, allowing us not only to model microstates with helical segments separated by coiled segments but also heteropolymers, that is, polymers which have peptide segments with different  $\kappa$  values. Moreover, the nearest-neighbor model can accurately represent  $\alpha$ -helix formation when coupling is modest, i.e., when  $\tau$  is small.

The transfer matrix we'll utilize is given as

$$T = \begin{bmatrix} \kappa\tau & 1 \\ \kappa & 1 \end{bmatrix} \quad (8.1.7)$$

where the columns of  $T$  represent the Boltzmann factor associated with the helical and coiled configurations, respectively, contingent on the conformation of the adjacent residues. To build the partition function we need to generate  $2^N$  terms, each representing the possible microstate of a particular residue, either helical or coiled. This is done by multiplying  $T$  by itself  $N$  times. Ultimately, in order to attain the scalar partition function it can be shown that

$$Q = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} \kappa\tau & 1 \\ \kappa & 1 \end{bmatrix}^N \begin{bmatrix} 1 \\ 1 \end{bmatrix} \quad (8.1.8)$$

where the row vector eliminates the top row of  $T^N$ , and the column vector combines remaining terms in the bottom row into a single sum. Barrick provides an example of utilizing Equation (8.1.8) for an  $N = 10$  homopolymer and I think the equation is kinda pretty and also provides some intuition behind the various combinations that are formed in the nearest-neighbor model, so I'm gonna use that example here as well, factoring slightly different than is provided on page 391 of Barrick. For an  $N = 10$  homopolymer,

$$\begin{aligned} Q = & 1 \\ & + 10\kappa \\ & + 9\kappa^2(4 + \tau) \\ & + 8\kappa^3(7 + 7\tau + \tau^2) \\ & + 7\kappa^4(5 + 15\tau + 9\tau^2 + \tau^3) \\ & + 6\kappa^5(1 + 10\tau + 20\tau^2 + 10\tau^3 + \tau^4) \\ & + 5\kappa^6\tau(1 + 10\tau + 20\tau^2 + 10\tau^3 + \tau^4) \\ & + 4\kappa^7\tau^3(5 + 15\tau + 9\tau^2 + \tau^3) \\ & + 3\kappa^8\tau^5(7 + 7\tau + \tau^2) \\ & + 2\kappa^9\tau^7(4 + \tau) \\ & + \kappa^{10}\tau^9 \end{aligned}$$

A few things to notice: 1) The sum of the coefficients in each row of the equation above sum to the the corresponding value in the 10th row of Pascal's triangle. That is, for row 5 in the equation above (taking the

first row to be row 0) with 5 helical residues, hence the factor of  $\kappa^5$ , the coefficients sum to

$$6(1 + 10 + 20 + 10 + 1) = \binom{10}{5} = 252$$

2) The partition function is symmetric with respect to the number of ways to arrange the helical coils in the polymer which connects directly to Pascal's triangle at what we just mentioned about the coefficients of the terms in each row. 3) Lastly, the ways of arranging the helical residues and the coefficients that come about for each term are a result of the order of the coupling constant,  $\tau$ . Notice that as the number of helices increases in the expression above, the order of  $\kappa$  increases linearly and doesn't depend on the number of ways to arrange the residues. In contrast, the coefficients of  $\tau$  (within the parentheses) vary drastically depending on how many helices are present, and in particular, they vary with the  $N$ th row of Pascal's triangle. That is all to say, the expressions for the partition function could be determined analytically without needing to go through all the matrix multiplication, all that it would require is some cheeky combinatorics and more willpower than is typically necessary than for anything else in this class.

With some newfound intuition for the partition function of the nearest-neighbor model we can analyze the predicted fractional helicity of a polymer under this model. Just as in the case of the zipper model, the fractional helicity can be expressed as a summation over each possible microstate with  $j$  helical residues:

$$\langle f_H \rangle = \frac{1}{N} \sum_{j=1}^N j p_j$$

Now, recall Equation (8.1.5) which contains a similar expression for the fractional helicity of a polymer under the zipper model. The  $(N - j + 1)$  term represents all of the combinations of helical residues that are permitted under this model. In contrast to this case, however, we've seen how this combinatorial coefficient for the nearest-neighbor model will be slightly more complex. So, we'll simplify our lives by expressing this coefficient as  $f(\tau, j, N)$ , indicating that it's a function of  $\tau$ ,  $j$ , and  $N$ . Hence, the fractional helicity becomes

$$\begin{aligned} \langle f_H \rangle &= \frac{1}{N} \sum_{j=1}^N j f(\tau, j, N) p_j \\ &= \frac{1}{NQ} \sum_{j=1}^N f(\tau, j, N) j \kappa^j \\ &= \frac{\kappa}{NQ} \sum_{j=1}^N f(\tau, j, N) \frac{d(\kappa^j)}{d\kappa} \\ &= \frac{\kappa}{NQ} \frac{d}{d\kappa} \sum_{j=1}^N f(\tau, j, N) (\kappa^j) \\ &= \frac{\kappa}{NQ} \frac{dQ}{d\kappa} \end{aligned} \tag{8.1.9}$$

Equation (8.1.9) is the fractional helicity of a polymer under the nearest-neighbor model. Similar to the derivations of some of the partition functions and fractional helicity expressions above, the derivative originally introduced in the derivation of Equation (8.0.6) was utilized in line 3.

Here is a list of the key results for the nearest-neighbor model:

$$Q = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} \kappa\tau & 1 \\ \kappa & 1 \end{bmatrix}^N \begin{bmatrix} 1 \\ 1 \end{bmatrix} \text{ is the partition function for the nearest-neighbor model.}$$

$p_i = \frac{f(\tau, i, N) \kappa^i}{Q}$  where  $f(\tau, i, N)$  is the really weird coefficient that isn't easy to express combinatorially, is the probability of there being  $i$  helices in a peptide of  $N$  residues.



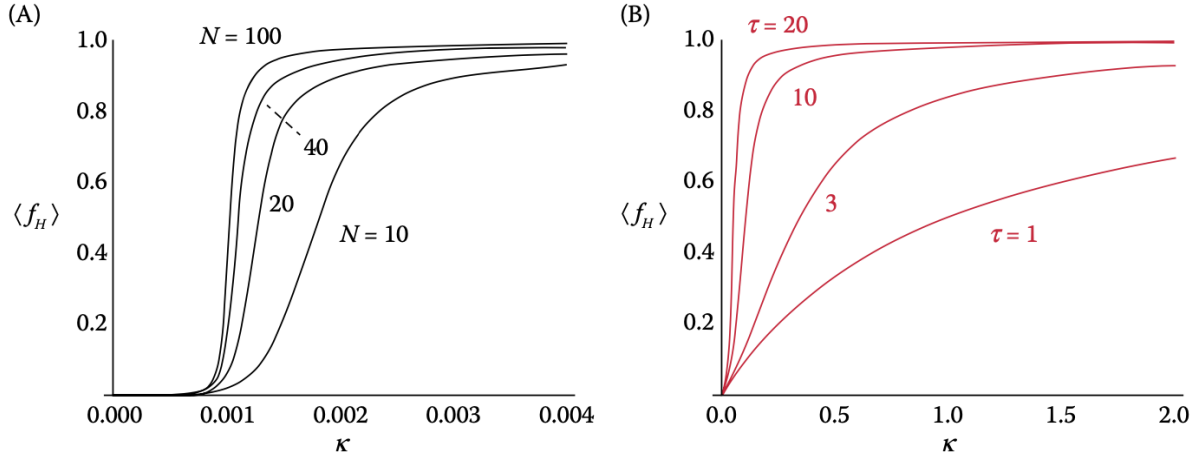


Figure 8.4: The shapes of the graphs of fractional helicity versus  $\kappa$  as the length of the peptide chain changes and as the coupling constant  $\tau$  changes are similar for the zipper model and nearest-neighbor model. The contrast lies in the shapes of the plots which vary  $\tau$ : For  $\tau = 1$  in figure above, a rectangular hyperbola appears which agrees with our intuition about cooperativity. Recall that for the zipper model the case of  $\tau = 1$  leads to inaccurate results, as expected. The nearest-neighbor model remedies those discrepancies.

$\langle f_H \rangle = \frac{\kappa}{NQ} \frac{dQ}{d\kappa}$  is a closed-form solution to the fractional helicity of a polymer under the zipper model.

Before ending our discussion on  $\alpha$ -helix formation I'll extend the nearest-neighbor model approach to a heteropolymer which will accommodate variation in a peptide sequence. In principle, differences in the transfer matrix for this model could arise due to variations in  $\kappa$  or in  $\tau$  (or both) but in practice it is far simpler to restrict effects on the transfer matrix to only  $\kappa$ . Then, our matrix becomes

$$T = \begin{bmatrix} \kappa_i \tau & 1 \\ \kappa_i & 1 \end{bmatrix}$$

where  $\kappa_i$  represents the Boltzmann factor for some residue on a polymer. Barrick uses the example of an  $\alpha$ -helix found in the myoglobin of sperm whales on page 393, a protein which houses  $N = 24$  residues. Finding the partition function by hand is unwieldy, yet trivial to a computer which is why I'll leave that calculation to you, in case you're interested. Additionally, variation in  $T$  creates a scenario where the matrix product does not easily factor into something compact leading to messy expressions for the partition function and fractional helicities of the protein.

## 8.2 Flory Theory

Paul Flory was a smart man, smarter than many of us will ever be. He was among one of the first scientists to prove that polymers are covalently linked macromolecules and went on to show that these covalent bonds are responsible for the principle differences between polymers and their monomeric constituents. He introduced *Flory theory* which addressed the problem of modeling real conformations of polymer chains using estimates for both the energetic and entropic contributions. Surprisingly, this simple model is incredibly accurate for real polymers. Although, it may be shown that this accuracy is due the cancellation of errors across the energetic and entropic terms. As we'll see, Flory theory *overestimates* both the the energetic and entropic contributions to the free energy, and since these contributions increase and decrease the free energy, respectively, their influences effectively cancel one another out.

To begin our discussion on Flory theory we'll first establish some basic definitions and parameters. In the most basic sense, we can consider a polymer as a long molecule consisting of repeating monomers linked together by bonds. Define the bond vector between any adjacent monomers as  $\vec{\tau}$  with magnitude  $||\vec{\tau}|| = b$ .

Additionally, we can define the end-to-end distance of the polymer as  $\vec{R} = \sum_i \vec{\tau}_i$  with magnitude  $||\vec{R}|| = R$ . The distinction of making  $\vec{\tau}$  and  $\vec{R}$  vectors is important because the bond between any two monomers can be pointing in any direction. Although, since the length of the bond between any two monomers will be constant, normally we won't have to worry about direction.

We can use a 1-dimensional monomer as a motivating example for this section. Each monomer can move in one of two directions, either "forward" or backward." Since this choice is random, the situation is effectively that of flipping a coin. So, the distribution of directions for each vector (in other words, how many ways does the monomer move forwards or backwards over the entire polymer) follows a binomial distribution. For a polymer of length  $N$  with  $N = n_1 + n_2$ , where  $n_1$  indicates the number of times a monomer is moving in direction 1 and  $n_2$  is defined similarly for the other direction, the number of ways for this polymer to be arranged is

$$W = \frac{N!}{n_1!n_2!}$$

If we define  $R/b = L$  as the displacement of the polymer (the distance from the beginning to the end of the polymer), then we have  $L = n_1 - n_2$  which implies  $(N + L)/2 = n_1$  and  $(N - L)/2 = n_2$  and we can rewrite the number of microstates for this 1-dimensional polymer as

$$W = \frac{N!}{(\frac{N+L}{2})!(\frac{N-L}{2})!} \quad (8.2.1)$$

Now we can use Stirling's approximation to write this in a more computationally friendly manner. First,

$$\ln W = N \ln N + N \ln 2 - \frac{N+L}{2} \ln(N+L) - \frac{N-L}{2} \ln(N-L)$$

Here we'll assume that  $N$  is large so that  $N \gg L/N$ . Moreover, define  $\varepsilon = L/N$  so that our expression may be simplified as,

$$\ln W = N \ln N + N \ln 2 - \frac{N(1+\varepsilon)}{2} \ln [N(1+\varepsilon)] - \frac{N(1-\varepsilon)}{2} \ln [N(1-\varepsilon)]$$

Here I took advantage of the fact that

$$\left(\frac{\frac{1}{N}}{\frac{1}{N}}\right) \frac{N+L}{2} = \frac{1+\frac{L}{N}}{2/N} = \frac{N}{2}(1+\varepsilon)$$

to make the first substitution above, and used a similar technique for the remaining expressions. The introduction of  $\varepsilon$  will prove useful because of the *quadratic approximation to*  $\ln(1+x)$ <sup>6</sup> (that's not a power of 6 it's a footnote). It's some pretty straightforward calculus to arrive at the approximation, so I'll just do it here quickly:

Recall that any second-order approximation can be modeled as

$$T_2(x) = f(x_0) + f'(x_0)(x - x_0) + \frac{f''(x_0)(x - x_0)^2}{2!}$$

where  $x_0$  is the point at which we're centering the approximation ( $x_0 = \varepsilon_0 = 0$  in this case) and  $f(x)$  is the

---

<sup>6</sup>We only care about the quadratic approximation and not any other higher order terms because the accuracy of the approximation increases negligibly once adding the third-, fourth-, fifth-order terms, etc.

function of interest ( $f(x) = \ln(1+x)$  in this case). Finding these derivatives and plugging in  $\varepsilon_0 = 0$  affords

$$\begin{aligned} T_2(x) &= \ln(1+\varepsilon_0) + \frac{1}{1+\varepsilon_0}(\varepsilon - \varepsilon_0) + \left(-\frac{1}{(1+\varepsilon_0)^2}\right)\frac{(\varepsilon - \varepsilon_0)^2}{2!} \\ &= \ln(1+0) + \frac{1}{1}(\varepsilon) + \left(-\frac{1}{(1)^2}\right)\frac{\varepsilon^2}{2!} \\ &= \varepsilon - \frac{\varepsilon^2}{2} \end{aligned}$$

Okay, back to the chemistry stuff. With this approximation we can rewrite our expression for  $\ln W$  as

$$\begin{aligned} \ln W &= N \ln N + N \ln 2 - \frac{N(1+\varepsilon)}{2} \ln [N + \varepsilon - \varepsilon^2/2] - \frac{N(1-\varepsilon)}{2} \ln [N - \varepsilon - \varepsilon^2/2] \\ &= N(\ln N + \ln 2) - \frac{N}{2} \left[ \ln N + \varepsilon - \varepsilon^2/2 + \varepsilon \ln N + \varepsilon^2 - \varepsilon^3/2 + \ln N - \varepsilon - \varepsilon^2/2 - \varepsilon \ln N + \varepsilon^2 + \varepsilon^3/2 \right] \\ &= N(\ln N + \ln 2) - \frac{N}{2} \left[ 2 \ln N + \varepsilon^2 \right] \\ &= N \ln N + N \ln 2 - N \ln N - \frac{N\varepsilon^2}{2} \\ &= N \ln 2 - \frac{N\varepsilon^2}{2} \\ &= N \ln 2 - \frac{L^2}{2N} = N \ln 2 - \frac{R^2}{2Nb^2} \end{aligned}$$

Thus,

$$\begin{aligned} W &= \exp \left\{ N \ln 2 - \frac{R^2}{2Nb^2} \right\} \\ &= 2^N e^{-R^2/2Nb^2} \end{aligned} \tag{8.2.2}$$

is the number of microstates for this random walk 1-dimensional polymer. If we wanted to consider the probability of any microstate, we'd be interested in the quantity

$$\frac{W}{2^N} = e^{-R^2/2Nb^2}$$

Upon further inspection, however, notice that the right-hand side of this equation is *unnormalized*. We can normalize the distribution by integration over the support of the possible values for  $R$ . Since  $\vec{R}$  can point in the positive or negative direction in the case of 1-dimension,  $R$  (the magnitude) can be either positive or negative and therefore the support of  $R$  is from  $-\infty$  to  $\infty$ . So,

$$\int_{-\infty}^{\infty} e^{-R^2/2Nb^2} dR = \sqrt{2\pi Nb^2}$$

which is exactly a Gaussian integral. I cover this sort of evaluation in Section ?? if you're interested. Thus, the probability distribution for the length of this 1-dimensional random walk polymer is

$$P(R) = \frac{e^{-R^2/2Nb^2}}{\sqrt{2\pi Nb^2}} \tag{8.2.3}$$

which is exactly a normal distribution.

### 8.2.1 The Troubling Case of a 3D Polymer

The logic followed for finding the probability distribution of the end-to-end distance for a random walk polymer in one-dimension, Equation (8.2.3), can be applied identically to the case of a three-dimensional polymer by

considering the movement in each of the possible three directions to be independent of one another. More technically, we would say that the movement in any of the  $x$ -,  $y$ -, and  $z$ -direction is *isotropic*. Then, the probability distribution for  $R$  in three dimensions is given by

$$\begin{aligned} P(R) &= P(R_x)P(R_y)P(R_z) = \left(\frac{e^{-R_x^2/2Nb^2}}{\sqrt{2\pi Nb^2}}\right)\left(\frac{e^{-R_y^2/2Nb^2}}{\sqrt{2\pi Nb^2}}\right)\left(\frac{e^{-R_z^2/2Nb^2}}{\sqrt{2\pi Nb^2}}\right) \\ &= \frac{e^{-3(R_x^2+R_y^2+R_z^2)/2Nb^2}}{(2\pi Nb^2/3)^{3/2}} \\ &= \left(\frac{3}{2\pi Nb^2}\right)^{3/2} e^{-3R^2/2Nb^2} \end{aligned}$$

Here, I've adopted the notation  $R = (R_x, R_y, R_z)$  to simplify the expression. Also, note that since we assumed that each of the directions are spatially isotropic with one another, the overall variance of the random walk must remain the same as if it were one-dimensional yet be distributed across three directions. Hence, the variances are given as

$$\langle R_x^2 \rangle = \langle R_y^2 \rangle = \langle R_z^2 \rangle = \frac{Nb^2}{3}$$

which accounts for the factor of  $1/3$  in each of the expressions.<sup>7</sup> However, this expression is not our final answer for the probability density. In the case of one dimension, the endpoint of the polymer chain did not have any degrees of freedom. That is, for a predetermined end-to-end vector  $\vec{R}$  there is only point for the end of the polymer to exist. This is in contrast to the three-dimensional case for which  $\vec{R}$  could exist *anywhere on the surface of a sphere*, centered at the tail of  $\vec{R}$ .<sup>8</sup> Thus, the probability density of the end-to-end distance for the three-dimensional random walk polymer must be scaled by the surface area of this sphere, given as

$$P(R) = 4\pi R^2 \left(\frac{3}{2\pi Nb^2}\right)^{3/2} e^{-3R^2/2Nb^2} \quad (8.2.4)$$

where  $R$  is the magnitude of the end-to-end vector.

We could have also arrived at Equation (8.2.4) beginning from entropy for the same type of polymer. Using Equation (8.2.2) as a template, the number of microstates for the three dimensional polymer may be expressed as

$$W = 4\pi R^2 e^{-3R^2/2Nb^2}$$

where the  $4\pi R^2$  takes the place of the  $2^N$  term as the scaling factor in three dimensions, and the exponential is raised to the power of 3 to account for the dimension as well. Then, the entropy of this polymer is found using Boltzmann's equation:

$$\begin{aligned} S &= k_B \ln W \\ &= k_B \ln(4\pi R^2 e^{-3R^2/2Nb^2}) \\ &= \frac{-3k_B R^2}{2Nb^2} + k_B \ln(4\pi R^2) \end{aligned}$$

The Helmholtz free energy which will take the place of the energy in our Boltzmann factor becomes

$$\begin{aligned} A &= -TS \\ &= -T \left[ \frac{-3k_B R^2}{2Nb^2} + k_B \ln(4\pi R^2) \right] \\ &= \frac{3k_B T R^2}{2Nb^2} - k_B T \ln(4\pi R^2) \end{aligned}$$

<sup>7</sup>The variance is equal to the second moment of the distribution in this case because the mean of the distribution is zero.

<sup>8</sup>The two dimensional analogue to this would be scaling the possible endpoints by the surface area of a circle.

which affords the Boltzmann factor for this polymer:

$$\begin{aligned} e^{-A/k_B T} &= \exp \left\{ - \left( \frac{3k_B T R^2}{2Nb^2} - k_B T \ln(4\pi R^2) \right) \right\} \\ &= \exp \left\{ - \frac{3R^2}{2Nb^2} + \ln(4\pi R^2) \right\} \\ &= 4\pi R^2 e^{-3R^2/2Nb^2} \end{aligned}$$

Thus, after properly normalizing we arrive at the probability density for the end-to-end distance of the three dimensional random walk polymer as

$$P(R) = 4\pi R^2 \left( \frac{3}{2\pi Nb^2} \right)^{3/2} e^{-3R^2/2Nb^2} \quad (8.2.5)$$

which agrees Equation (8.2.4).

### 8.2.2 Self-Avoiding Polymers

Our discussion of random walk polymers up until this point has focused on those which are driven entirely by entropy. Now, we introduce the idea of a *self-avoiding polymer*, one with a nonzero free energy term that depends on repulsion between monomers. Returning to the simplest version of a three-dimensional polymer with an entropy given by,

$$S(R) = \frac{3k_B R^2}{2Nb^2} \quad (8.2.6)$$

Flory suggested introducing a term representing the internal energy of the polymer which takes the form

$$\begin{aligned} A &= U - TS \\ &= \frac{vN^2}{R^3} - T \left( C - \frac{3k_B R^2}{2Nb^2} \right) \end{aligned} \quad (8.2.7)$$

where the  $N^2/R^3$  term is representative of the density of monomer pairs within the volume created by the polymer,  $v$  is a proportionality constant, and  $C$  is some constant to represent the ground state energy of the polymer;  $N^2$  is indicative of the pairwise interaction and  $R^3$  is directly proportional to the volume of the ‘sphere’ surrounding the polymer. This is why the interaction ‘per’ volume can be thought as a density. Intuitively, the idea of this repulsive energy term is similar to steric hindrance. It’s important to note that  $v$  is positive so that the term  $vN^2/R^3$  is always positive as well; This guarantees that the energy term will indeed be repulsive.

With this new expression for the internal free energy we can compute the equilibrium length of the polymer. At equilibrium, the free energy will be *minimized* and so  $\partial A/\partial R = 0$ :

$$\begin{aligned} \frac{\partial A}{\partial R} &= \frac{\partial}{\partial R} \left[ \frac{vN^2}{R^3} - T \left( C - \frac{3k_B R^2}{2Nb^2} \right) \right] \\ 0 &= \frac{-3vN^2}{R^4} + \frac{6k_B T R}{2Nb^2} \\ \frac{vN^2}{R^4} &= \frac{k_B T R}{Nb^2} \\ R &= \left( \frac{vb^2}{k_B T} \right)^{1/5} N^{3/5} \end{aligned} \quad (8.2.8)$$

This result for the end-to-end length of the polymer using a simple model asserts that the length is proportional to the number of monomers to the power of 0.6, that is,  $N^{3/5}$ . Experimentally, the accepted result for the exponent is 0.588, incredibly close to that predicted by Flory. At this point it’s important to recognize that

we would not have achieved this result had we assumed the energy of interaction between monomers could be favorable, that is, allowing  $v$  to be negative. It's a subtle difference, and modeling inter-polymer interactions as favorable would be weird, but important to understand to reinforce our understanding nonetheless.

Notice the temperature dependence of the equilibrium length for the polymer. When we increase the temperature of the polymer, the entropic term of the free energy in Equation (8.2.7) has a greater impact. Additionally, from Equation (8.2.8) we see that the equilibrium length of the polymer decreases as temperature increases. Thus, using Equation (8.2.6) the entropy of the polymer must also decrease with an increase in temperature and therefore the overall free energy of the polymer increases, corresponding to a greater number of monomer-monomer interactions which goes hand-in-hand with a smaller polymer size. That is all to say, our intuition is correct!

This result prompted a more generalized version of the free energy for a self-avoiding polymer in  $d$  dimensions. Typically, as chemists, nobody really cares about dimensions greater than three because why would you. However, I guess Flory was a physicist so he was interested in this. The power law we desire is relatively intuitive, though, using a similar argument as we did above regarding the density of interactions. Note that the volume of an  $n$ -dimensional sphere is directly proportional to the radius of the sphere to the  $n$ th power. Thus, the term introduced to the free energy in Equation (8.2.7) can be rewritten as  $vN^2/R^d$  for any  $d$  dimensions. In addition, we require that the entropy term be scaled by a factor of  $d$  which can be derived from the Boltzmann equation (at least I'm pretty sure you could derive it from the Boltzmann equation). Thus, a generalized expression for the free energy of a self-avoiding random walk polymer in  $d$  dimensions is given as

$$A = \frac{vN^2}{R^d} - T \left( C - \frac{dk_B R^2}{2Nb^2} \right) \quad (8.2.9)$$

Then, we can model the equilibrium length of the polymer to the number of monomers in the chain relation as

$$R \propto N^\nu, \quad \nu = \frac{3}{d+2} \quad (8.2.10)$$

where  $\nu = 3/5$  was our result for three dimensions in Equation (8.2.8) which agrees with our result from Equation (8.2.10) for  $d = 3$ .

Real quick before talking about binding equilibria, the theoretical result that the internal energy for a self-avoiding random walk polymer is proportional to  $1/R^d$  can be rationalized if we think of a polymer as a snake from Snake (like the video game). The game Snake becomes *a lot* easier as we add more dimensions because there are more directions to move and therefore less ways of getting "trapped." Hence, there are less arrangements of the polymer in which unfavorable monomer-monomer interactions occur in higher dimensions and the internal energy term decreases.

## 8.3 Binding Equilibria

Binding reactions and their equilibria are central to nearly biochemical process. From the binding of THC to cannabinoid receptors in your brain to the HGH injected by bodybuilders, drug binding is a large part of biological and physical science.

We'll begin by analyzing a simple bimolecular reaction involving the binding of a single ligand,  $x$ , to the active site of a macromolecule,  $M$ . This reaction can be written as



where the equilibrium constant is given by

$$K_{eq} = \frac{[Mx]}{[M][x]} = e^{-\Delta\tilde{G}_{rxn}/RT} = K_d^{-1} \quad (8.3.2)$$

$K_d$  is the *dissociation constant* and used primarily by biochemists because it has “units” of molarity.<sup>9</sup> Moreover,  $K_d$  represents the free ligand concentration at which the molecule is *half-saturated*, when  $[Mx] = [M]$ .

The relationships outlined in Equation (??) provide simple thermodynamic descriptions of a single-site binding event. However, to be useful in an experiment they must be able to be connected to actual binding data. The most common of these statistics are *fractional saturation*,  $\langle f_b \rangle$ , and *average ligation number*,  $\langle x_b \rangle$ . The fractional saturation is defined as the fraction of macromolecular binding sites that have ligand bound and can be expressed as

$$\langle f_b \rangle = \frac{[Mx]}{[M] + [Mx]} \quad (8.3.3)$$

Similarly, the average ligation number is the average number of ligands bound per macromolecule and is related to the fractional saturation by

$$\langle f_b \rangle = \frac{\langle x_b \rangle}{s}$$

where  $s$  is the number of active sites on the macromolecule. The fractional saturation can be related to the equilibrium constant with relative ease using Equation (8.3.2):

$$\begin{aligned} \langle f_b \rangle &= \frac{[Mx]}{[M] + [Mx]} \\ &= \frac{K_{eq}[M][x]}{[M] + K_{eq}[M][x]} \\ &= \frac{K_{eq}[x]}{1 + K_{eq}[x]} \end{aligned} \quad (8.3.4)$$

Equation (8.3.4) is important and incredibly useful because it relates experimentally observable quantities,  $\langle f_b \rangle$  and  $[x]$ , to a thermodynamically relevant quantity, the equilibrium constant. Notice that this expression for  $\langle f_b \rangle$  more clearly illustrates how a plot of  $\langle f_b \rangle$  vs.  $[x]$  is a *rectangular hyperbola*.

As with conformational transitions (covered in Chapter 5), the midpoint of the binding curve is an important parameter with direct connections to thermodynamics. We can evaluate the midpoint of the binding curve by allowing  $\langle f_b \rangle = 0.5$ . Using Equation (8.3.4), then,

$$\begin{aligned} 0.5 &= \frac{K_{eq}[x]_m}{1 + K_{eq}[x]_m} \\ [x]_m &= \frac{1}{K_{eq}} = K_d \end{aligned} \quad (8.3.5)$$

Thus, we see that the numerical value of the equilibrium constant strongly influences the shape of the resultant binding curve. This result is similar to a titration curve for acid-base chemistry, where an acid is half-protonated when  $pH = pK_a$ . Plotting the fractional saturation curve affords some nice curves and allows us to see how the binding constant,  $K_{eq}$ , affects the shape of the graph. These graphs can be found in Figure 8.5.

Within an experiment we won't ever actually measure the fractional saturation directly. Instead, some signal  $Y_{obs}$  is observed and recorded. In particular,  $Y_{obs}$  is assumed to be a signal originating from a population-

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<sup>9</sup>In reality, equilibrium constants are never given a unit. So, it stands to reason that  $K_d$  is used because of its apparent dimensionality which makes it easier to talk about.

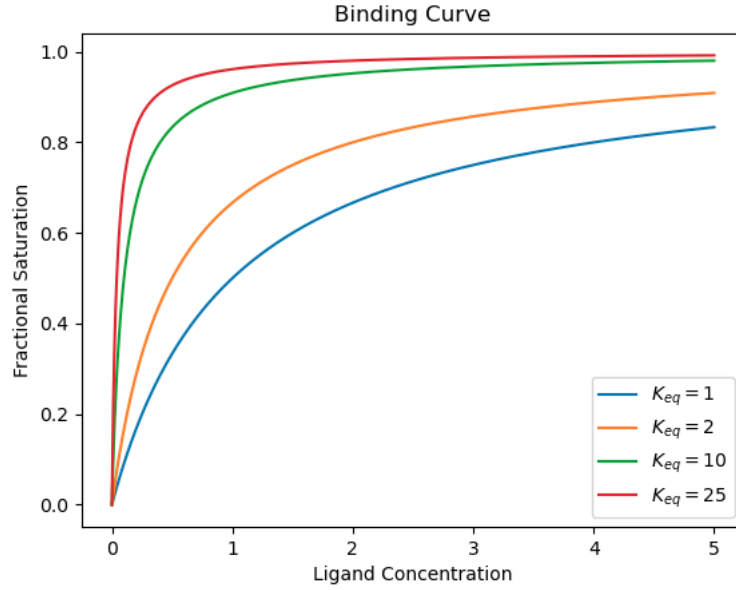


Figure 8.5: Binding curve of  $\langle f_b \rangle$  vs.  $[x]$  for multiple equilibrium constants. The larger the equilibrium constant, the more affinity the ligand has for the active site on the molecule and the more steep the transition in the curves above. The curve which reaches  $\langle f_b \rangle = 1$  the fastest (the red curve) would be the strongest binder and the one which reaches a fractional saturation of 1 the most slowly (the blue curve) is the weakest binder.

weighted average of unbound and bound macromolecule, expressed as

$$\begin{aligned}
 Y_{obs} &= Y_{free}f_{free} + Y_{bound}f_{bound} \\
 &= Y_{free}(1 - f_{bound}) + Y_{bound}f_{bound} \\
 &= Y_{free} + (Y_{bound} - Y_{free})f_{bound} \\
 &= Y_{free} + \Delta Y \left( \frac{K_{eq}[x]}{1 + K_{eq}[x]} \right)
 \end{aligned} \tag{8.3.6}$$

Equation (8.3.6) offers a way of indirectly measuring the fractional saturation,  $\langle f_b \rangle$ . Also, above we defined  $\Delta Y = Y_{bound} - Y_{free}$  which is the *amplitude*, or better yet *dynamic range*, of the data and is indicative of the total deflection swept out by the binding curve. Binding processes which give rise to a large amplitude provide greater confidence in our measurements for the fractional saturation and the equilibrium constant.

In most ligand binding experiments, a solution of macromolecule M is prepared at a known concentration and then a specific amount of ligand x is added at a known concentration. So, although we know the total amounts of ligand and macromolecule, once they're combined and the binding reaction begins its difficult to determine the concentrations of either. By invoking the conservation of mass to the reaction in Equation (8.3.1) we can say that

$$\begin{aligned}
 [x]_{tot} &= [x] + [Mx] \\
 [M]_{tot} &= [M] + [Mx]
 \end{aligned}$$

are the total concentrations of the ligand and macromolecule, respectively. Then, we can rewrite the equilibrium constant in Equation (8.3.2) using the known parameters as

$$K_{eq} = \frac{[Mx]}{[M][x]} = \frac{[Mx]}{([M]_{tot} - [Mx])([x]_{tot} - [Mx])}$$



which can be rewritten as a quadratic in  $[Mx]$  and solved accordingly:

$$\begin{aligned}
 [Mx] &= K_{eq}([M]_{tot} - [Mx])([x]_{tot} - [Mx]) \\
 0 &= K_{eq}([M]_{tot} - [Mx])([x]_{tot} - [Mx]) - [Mx] \\
 &= [Mx]^2 - \left([M]_{tot} + [x]_{tot} + \frac{1}{K_{eq}}\right)[Mx] + [M]_{tot}[x]_{tot} \\
 [Mx] &= \frac{[M]_{tot} + [x]_{tot} + (1/K_{eq}) \pm \sqrt{([M]_{tot} + [x]_{tot} + (1/K_{eq}))^2 - 4[M]_{tot}[x]_{tot}}}{2}
 \end{aligned} \tag{8.3.7}$$

Notice that we “created” this quadratic with the initial substitutions into the expression for the equilibrium constant and with that introduced some extraneous answers. To determine which of (+) or (−) we want after applying the quadratic formula we can evaluate our new expression for  $[Mx]$  in Equation (8.3.7) at  $[x]_{tot} = 0$  M:

$$\begin{aligned}
 [Mx] &= \frac{[M]_{tot} + (1/K_{eq}) \pm \sqrt{([M]_{tot} + (1/K_{eq}))^2}}{2} \\
 &= \frac{[M]_{tot} + (1/K_{eq}) \pm ([M]_{tot} + (1/K_{eq}))}{2}
 \end{aligned}$$

Clearly, when  $[x]_{tot} = 0$  M,  $[Mx] = 0$  M must also be true because there is no ligand to bind. Hence, we’ll be interested in the “minus” of ( $\pm$ ) in our quadratic. Then, plugging this result into Equation (8.3.6) for  $Y_{obs}$  affords

$$Y_{obs} = Y_{free} + \Delta Y \left( \frac{[M]_{tot} + [x]_{tot} + (1/K_{eq}) \pm \sqrt{([M]_{tot} + [x]_{tot} + (1/K_{eq}))^2 - 4[M]_{tot}[x]_{tot}}}{2[M]_{tot}} \right) \tag{8.3.8}$$

### 8.3.1 Fluorescence Anisotropy

*Fluorescence anisotropy* is a phenomenon in which the light emitted by a fluorophore has unequal intensities along different axes of polarization.<sup>10</sup> When a fluorophore absorbs a photon an electron is excited to the excited state and, after a short waiting time, the electron emits that energy as either a photon (radiative emission) or as heat (non-radiative emission) and returns to the ground state. This excitation is associated with an *unequal* redistribution of electrons throughout the molecule such that only electrons which are oriented in the same way as the incoming light may be excited.<sup>11</sup>

If we limit our experiment to measuring only radiative emission (and disregarding the quantum yield, I suppose), the direction of the wave of light emitted by the excited fluorophore will change with respect to a few parameters, the most important of which (in our case) being the time that the electron stays in the excited state before being emitted. In the limit that the electron returns to the ground state immediately after being excited, that is, there is no waiting time, the direction of light will be *the exact same* as that absorbed. In the limit that the electron dawdles in the excited state, that is, the waiting time is long, there is a significant probability that the direction of the light which is emitted from the fluorophore is different from that absorbed. Typically, smaller fluorophores have shorter waiting times and larger fluorophores have longer waiting times. So, by measuring the type of light that the fluorophore emits and comparing it to the light which we initially shined at it, we can estimate how large or small the protein is!

Obviously, this model is very simplified. Fluorescence experiments can do a lot more than this, but this example utilizes how we might use it in the context of ligand binding. In fact, in the references there is a very

<sup>10</sup>*Anisotropy* is defined as “having a physical property that has a different value when measured in different directions.” A very simple example is wood which is stronger along the grain than across it. When we talk about fluorescence anisotropy we’re referring to asymmetric distribution of orientations for the waves of light emitted by the fluorophore upon excitation.

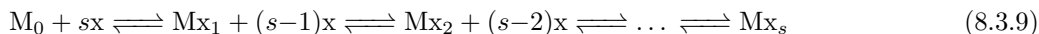
<sup>11</sup>The “orientation” with respect to an electron and a wave are seemingly unrelated at first. An electron has an associated spin whereas a wave has an associated... orientation. I like to think about it in terms of vectors: the vector associated with the electron has a direction determined by the *angular momentum* of the particle (in fact, this is one of the quantum numbers associated with each electron) and the vector associated with the wave is that normal to the “surface” formed by the wave. Then, light will be absorbed by the electron which has an angular momentum vector *in the same direction* as the normal vector to the wave.

informative book about all sorts of fluorescence experiments (and fluorescence anisotropy, of course) that I like enough to also draw your attention to here:

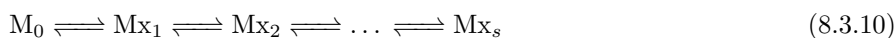
[https://link.springer.com/chapter/10.1007%2F978-0-387-46312-4\\_10](https://link.springer.com/chapter/10.1007%2F978-0-387-46312-4_10)

### 8.3.2 Numerous Binding Sites

Many macromolecules have multiple binding sites and the single-site scheme discussed up until this point proves insufficient in describing these systems, in addition to being mechanistically incorrect. Considering only a single type of ligand which can bind to some macromolecule,<sup>12</sup> we can represent the reaction with the following scheme,



or more simply



A key feature of macromolecule binding events is that they can be energetically coupled such that binding can either encourage or discourage the affinity of the macromolecule for ligand. This phenomenon is referred to as *cooperativity* (I'm pretty sure I already talked about it somewhere).

Assuming I have in fact talked about cooperativity somewhere else in this paper, we'll begin to draw some parallels between multisite binding phenomena and single-site binding. The fractional saturation for a molecule with multiple binding sites can be represented as a sum of the concentrations of all forms of macromolecule with ligand bound, times the fractional saturation of the macromolecule in each corresponding ligation state, divided by the total concentration of macromolecule. Symbolically,

$$\begin{aligned} \langle f_b \rangle &= \frac{\frac{1}{s}[Mx_1] + \frac{2}{s}[Mx_2] + \dots + \frac{s}{s}[Mx_s]}{[Mx_1] + [Mx_2] + \dots + [Mx_s]} \\ &= \frac{1}{s} \left( \frac{\sum_{k=1}^s k[Mx_k]}{\sum_{k=1}^s [Mx_k]} \right) \end{aligned}$$

This expression for the fractional saturation can be cumbersome. We can try and simplify it by substituting  $K_i[M][x]_i = [Mx]_i$  for each of the bound terms above, but even then we're left with many, difficult to measure quantities. So, instead, we can utilize the relationships given in Figure 8.6 to express each of the  $[Mx]_i$ 's with rearranged versions of the *overall binding constants* to yield

$$\begin{aligned} \langle f_b \rangle &= \frac{1}{s} \left( \frac{\beta_1[M_0][x] + 2\beta_2[M_0][x]^2 + \dots + s\beta_s[M_0][x]^s}{[M]_0 + \beta_1[M_0][x] + \beta_2[M_0][x]^2 + \dots + \beta_s[M_0][x]^s} \right) \\ &= \frac{1}{s} \left( \frac{\beta_1[x] + 2\beta_2[x]^2 + \dots + s\beta_s[x]^s}{\beta_1[x] + \beta_2[x]^2 + \dots + \beta_s[x]^s} \right) \end{aligned}$$

Notice that the denominator of the fractional saturation as its been expressed most simply is a simple polynomial in the ligand concentration,  $[x]$ . We can refer to this expression as the *binding polynomial*, defining

$$P = 1 + \beta_1[x] + \beta_1[x]^2 + \dots + \beta_s[x]^s = 1 + \sum_{i=1}^s \beta_i[x]^i \quad (8.3.11)$$

$P$  closely resembles expressions we've seen for partition functions in statistical mechanics, *except* for the fact that  $P$  is a polynomial and not a sum of exponentials. However, recall from Chapter 5, in Equation (4.1.21) we defined the chemical potential of a species in a solution. Using this expression we can relate the

<sup>12</sup>We'd refer to the macromolecule as being "homotropic" in this case. If the molecule was instead capable of binding all sorts of different ligands it would earn the title of "heterotropic."

(A)			(B)		
Stepwise reaction	Stepwise binding constant	Units	Overall reaction	Overall binding constant	Units
$M_0 + x \rightleftharpoons Mx$	$K_1 = \frac{[Mx]}{[M_0][x]}$	$M^{-1}$	$M_0 + x \rightleftharpoons Mx$	$\beta_1 = \frac{[Mx]}{[M_0][x]}$	$M^{-1}$
$Mx + x \rightleftharpoons Mx_2$	$K_2 = \frac{[Mx_2]}{[Mx][x]}$	$M^{-1}$	$M_0 + 2x \rightleftharpoons Mx_2$	$\beta_2 = \frac{[Mx_2]}{[M_0][x]^2} = K_1 K_2$	$M^{-2}$
...	...	...	...	...	...
$Mx_{s-1} + x \rightleftharpoons Mx_s$	$K_s = \frac{[Mx_s]}{[Mx_{s-1}][x]}$	$M^{-1}$	$M_0 + sx \rightleftharpoons Mx_s$	$\beta_s = \frac{[Mx_s]}{[M_0][x]^s} = \prod_{i=1}^s K_i$	$M^{-s}$

Figure 8.6: For a macromolecule with  $s$  binding sites, ligand binding can be described as a series of steps, each of which is the binding event of a single ligand, represented by part (A) of the figure. Alternatively, multisite binding can be described as a collection of overall binding reactions in which the reactants are  $i$  ligands and the product contains  $i$  bound ligands, represented in (B).

concentration of a species in solution to an exponential as

$$[x]^i = \left( e^{-(\mu_x^\circ - \mu_x)/RT} \right)^i \quad (8.3.12)$$

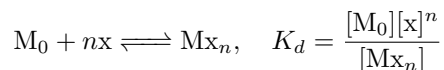
Substituting Equation (8.3.12) into the binding polynomial affords a partition function that allows the chemical potential of one of the reactants to vary, which is appropriate for a ligand binding experiment.<sup>13</sup> With  $P$  thoroughly defined, we can use it to concisely express the fractional saturation  $\langle f_b \rangle$  (for the last time):

$$\begin{aligned}
 \langle f_b \rangle &= \frac{1}{s} \left( \frac{\sum_{i=1}^s i \beta_i [x]^i}{P} \right) \\
 &= \frac{[x] \sum_{i=1}^s i \beta_i [x]^{i-1}}{sP} \\
 &= \frac{[x] \sum_{i=1}^s \beta_i (d[x]^i / d[x])}{sP} \\
 &= \frac{[x]}{sP} \frac{d \left( \sum_{i=1}^s \beta_i [x]^i \right)}{d[x]} \\
 &= \frac{[x]}{sP} \frac{d \left( 1 + \sum_{i=1}^s \beta_i [x]^i \right)}{d[x]} \\
 &= \frac{[x]}{sP} \frac{dP}{d[x]} = \frac{1}{s} \frac{d \ln P}{d \ln [x]} \quad (8.3.13)
 \end{aligned}$$

Equation (8.3.13) offers the fractional saturation of a macromolecule with multiple binding sites. Figure 8.7 illustrates the differences in shapes between the fractional saturation curves of macromolecules with two active sites, one of which is positively cooperative and the other of which is negatively cooperative.

### 8.3.3 The Hill Model

The Hill Model is one of the simplest models for cooperativity in ligand binding and was first introduced in an attempt to analyze the binding of oxygen to hemoglobin. Essentially, the Hill model assumes *infinite cooperativity* such that once a single ligand is bound to a multi-site molecule, all other binding sites are immediately bound as well. Schematically, this can be written as



<sup>13</sup>This is analogous to the partition function of the “grand canonical ensemble,” something that I hope I already had the chance to discuss in the chapter on Statistical Mechanics.

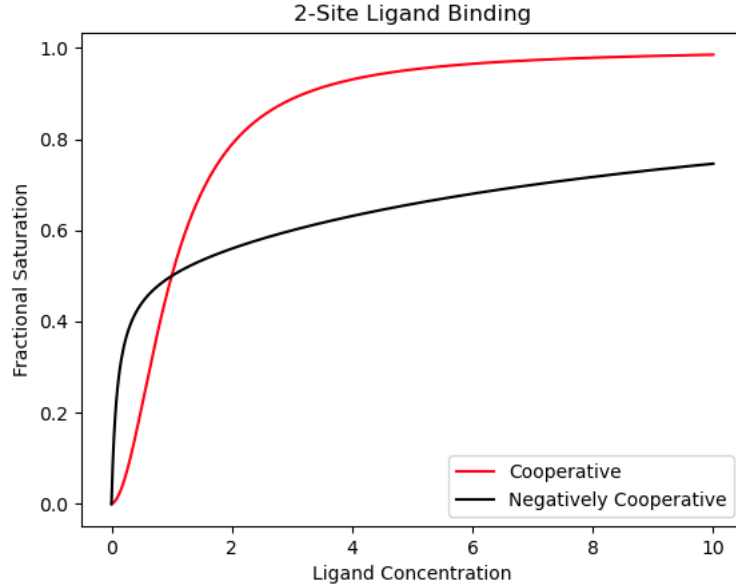


Figure 8.7: The curves shown above illustrate the shapes of the binding curves for a (positively) cooperative and negatively cooperative macromolecule with two binding sites (the shape holds for any number of  $n$  binding sites, though). The equilibrium constants for the cooperative binding are  $K_1 = 0.1 \text{ M}^{-1}$  and  $K_2 = 10 \text{ M}^{-1}$ . The equilibrium constants for the negatively cooperative binding are  $K_1 = 10 \text{ M}^{-1}$  and  $K_2 = 0.1 \text{ M}^{-1}$ .

where  $n$  is the number of active sites on the molecule and therefore also the number of ligands necessary for the reaction to proceed. Following a similar procedure as we did to derive the fractional saturation of a single-site macromolecule in Equation (8.3.4) we can show that the fractional saturation for a macromolecule following the Hill model is given by

$$\langle f_b \rangle = \frac{[x]^n}{K_d + [x]^n} \quad (8.3.14)$$

Historically,  $n$  is known as the *Hill constant*, and it increases with increasing cooperativity of a reaction. Thus, it provides a convenient and simple characterization for a ligand binding reaction. For  $n > 1$ , binding reactions are *positively cooperative*, for  $n < 1$ , binding reactions are *negatively cooperative*, and for  $n = 1$  binding reactions are *noncooperative*. It's important to note, however, that the Hill model is exactly that, *a model*. For example, the binding of diatomic oxygen to hemoglobin would have a Hill constant of  $n = 4$ . Experimentally, it's been determined that the binding curve fits  $n \approx 3$  more appropriately. Additionally, diseases which affect the blood can decrease the Hill constant of hemoglobin further, such as the genetic defects associated with sickle-cell anemia.

Equation (8.3.14) can be used to derive the *Hill plot* which affords more information about the thermodynamics of the binding reaction. Don't worry though, only a small amount of algebraic gymnastics is necessary to get us there

$$\begin{aligned} \langle f_b \rangle (K_d + [x]^n) &= [x]^n \\ \langle f_b \rangle K_d &= [x]^n (1 - \langle f_b \rangle) \\ \frac{\langle f_b \rangle}{1 - \langle f_b \rangle} &= \frac{[x]^n}{K_d} \\ \ln \left( \frac{\langle f_b \rangle}{1 - \langle f_b \rangle} \right) &= n \ln [x] - \ln K_d \end{aligned} \quad (8.3.15)$$

Equation (8.3.15)

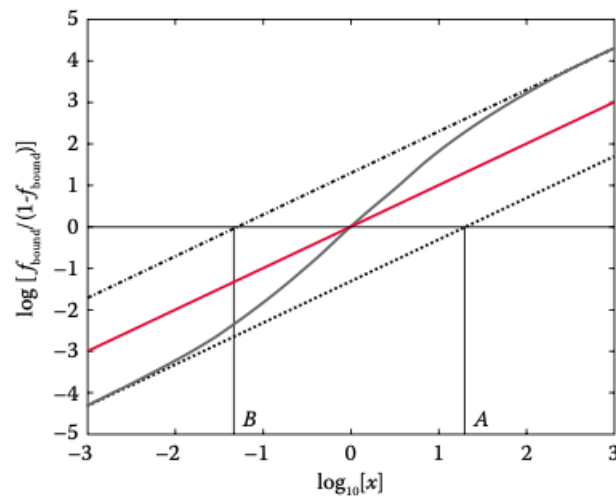


Figure 8.8: This is the Hill plot for a two-site macromolecule. Here we've used  $K_1 = 0.1 \text{ M}^{-1}$  and  $K_2 = 10 \text{ M}^{-1}$ . The Hill plot (in grey) limits to a slope of 1 along the dotted lines which represent limiting ligand concentrations. At these concentrations, binding appears as if to single-site macromolecules. At the midpoint, the slope of the binding curve is steeper than that of the reference line (in fact, the slope approaches 2), reflecting positive cooperativity. The case of negative cooperativity would have a grey curve which would look reflected over the red (reference) line.

## CHAPTER

## 9

# CHEMICAL KINETICS

### *Chemical Kinetics*

- *Scientist*

A key theme running through the advancement of chemical kinetics is complexity. It includes the investigation of how experimental conditions influence the speed of a reaction and inform us about a reaction's mechanism and transition state. In contrast to thermodynamics, kinetics affords a *rate of reaction*, not a direction.

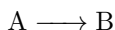
Chemical kinetics is one of the oldest branches of chemistry and is responsible for assigning rate constants to reactions and understanding the mechanisms behind chemical transformations. It is the 'macroscopic' treatment of the *time-evolution* of a system *not in equilibrium*. Hence, it allows us to differentiate between things which are actually impossible versus things that are incredibly slow, e.g., the conversion of glucose to water, carbon dioxide, and energy without any external motivation.

As a motivating example, consider the transformation of diamond to graphite,  $\text{C}_{(\text{d})} \rightleftharpoons \text{C}_{(\text{g})}$ . This reaction is exergonic with  $\Delta\tilde{G}_{\text{rxn}}^{\circ} \approx -2.9 \text{ kJ/mol}$ . So, we'd expect this reaction to occur spontaneously at room temperature... which it does. Then why is it we never see this decay into graphite during fancy dinner parties when everyone is wearing diamond jewelry? It's because the reaction takes a *very long time*.<sup>1</sup> Though, at exceptionally high temperatures we can observe this reaction with an appreciable rate. With this idea in mind we can add to our list of contrasts between thermodynamics and kinetics:

*Stability* refers to thermodynamics. Using our example of the decay from diamond to graphite, diamond is considered unstable whereas graphite is stable.

*Persistence* refers to kinetics. In this example, both diamond and graphite may be called persistent because the rate of decay from one phase to the other is immensely slow. The opposite of persistent is *transient*.

Kinetics is all about time-evolution and so we'll begin our kinetic description of a chemical reaction using differential equations. Consider the chemical transformation



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<sup>1</sup>So long, in fact, that the average domesticated turkey would have to survive  $10^8$  times longer than it would on average to ever witness the reaction take place.

We can express the rate of this reaction as

$$\text{rate} = \frac{d[\text{B}]}{dt}$$

By the law of conservation of energy, for every B that is formed there must be a corresponding A which disappears and we can therefore express the rate alternatively as

$$\text{rate} = -\frac{d[\text{A}]}{dt} \quad (9.0.1)$$

More generally, for any chemical reaction of the form  $a\text{A} + b\text{B} \longrightarrow g\text{G} + h\text{H}$  we can express the rate as

$$\begin{aligned} \text{rate} &= \frac{1}{\nu_{\text{A}}} \frac{d[\text{A}]}{dt} = \frac{1}{\nu_{\text{B}}} \frac{d[\text{B}]}{dt} = \frac{1}{\nu_{\text{G}}} \frac{d[\text{G}]}{dt} = \frac{1}{\nu_{\text{H}}} \frac{d[\text{H}]}{dt} \\ &= -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{g} \frac{d[\text{G}]}{dt} = \frac{1}{h} \frac{d[\text{H}]}{dt} \end{aligned}$$

where  $\nu_i$  are the reaction coefficients as defined in Section 5.2. Empirical evidence shows that the rates of reactions for chemical transformations of this form can be expressed as

$$\text{rate} = k[\text{A}]^x[\text{B}]^y \quad (9.0.2)$$

where  $k$  is the *rate constant* and the reaction is said to be  $x$ th order in A and  $y$ th order in B. Since the rate of a reaction must also have units of molarity per second, the units for the rate constant must change depending on the order of reaction and can be expressed concisely as  $\text{M}^{-(x+y-1)} \text{s}^{-1}$ .

Keep in mind that the *order* of a reaction is different from the *molecularity* of a reaction. The *molecularity* of a reaction is the number of molecules that come together to react in an *elementary* step of a reaction. It is equal to the sum of the stoichiometric coefficients of reactants. So, in the case of an elementary process, the molecularity and order of a reaction are the same. The subtle yet important difference between these two concepts may be expressed using a simple example. Consider the following two processes:

<i>Bimolecular</i>	<i>Unimolecular</i> "Activation"
$\text{A} + \text{B} \longrightarrow \text{P}$	$\text{A} \longrightarrow \text{I}$
	$\text{I} + \text{B} \longrightarrow \text{P}$

Here, A and B are reactants and I is some intermediate. The bimolecular reaction would be second-order overall and first-order with respect to both A and B, with a rate expression

$$\text{rate} = k[\text{A}][\text{B}]$$

Assuming that the activation step  $\text{A} \longrightarrow \text{I}$  is rate-limiting and that the formation of product P is rapid, the unimolecular reaction would be first-order overall, first order with respect to A, and zero-order with respect to B, with an expression for the rate as

$$\text{rate} = k[\text{A}]$$

A great example of a bimolecular process would be an SN2 reaction, which proceeds through a concerted backside attack. Similarly, an example of unimolecular process might be an SN1 reaction where the high-energy intermediate forms (oftentimes we think of a carbocation) before another reactant comes in to attack the intermediate. Another common unimolecular reaction would be an intramolecular reaction, such as the Cope rearrangement. A more rare type of reaction is a *termolecular* process in which three molecules simultaneously come together to react.

Another example which may illustrate the important difference between order and molecularity is the formation of amyloid- $\beta$  ( $\text{A}\beta$ ) which is found in the brains of people with Alzheimer's disease.  $\text{A}\beta$  can form

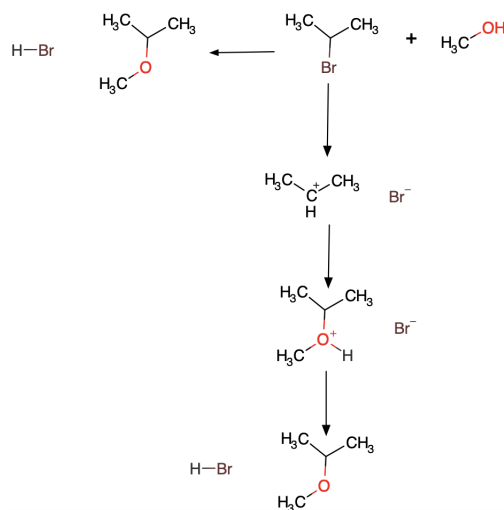
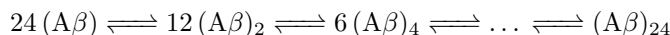


Figure 9.1: The difference between a bimolecular and unimolecular reaction. Above, the synthesis of 2-methoxypropane can happen through either an SN1 or SN2 reaction which have different rate laws.

complex oligomers, following a reaction scheme such as

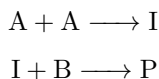


Needless to say, it's certainly not the case that 24 copies of  $A\beta$  come together at once to form the oligomer in a single step. Thus, it becomes more clear how the molecularity, the number of monomers coming together to form an intermediate complex in this scheme, can be much different from the empirically determined reaction order. A logical question, then, is which intermediates do form? Which steps of the process are rate-limiting?

The answer to these questions can *never* be proven, only supported or better yet disproven. Consider the following illustrative example: Suppose that for the simple reaction  $A + B \longrightarrow P$  we collect some data and seek to determine the mechanism by which the reaction proceeds.

$[A]_0$ (mM)	Initial $d[A]_0/dt$ (mM/s)
10	-0.1
20	-0.4
30	-0.9

If we suppose that the reaction is modeled by rate  $= k[A]^x[B]^y$ , the data would suggest that  $x = 2$ , consistent with the mechanism



but not the mechanism  $A + B \longrightarrow P$ . Of note is that fact that integer exponents are most common for rate laws and will always be the case for elementary reactions (in which the molecularity of the reaction and reaction order are the same). For complex processes, however, it is possible to have fractional exponents in the rate law.<sup>2</sup>

In the table of data for this experiment notice that we always collected *initial* concentrations. This is because we always know and can control the initial concentration of the starting species. So, we can also always be sure that when we measure the initial rate of reaction we are using the correct initial concentrations. In theory, the rate law is a *law* and can be used to estimate the rate at any time during the reaction. However, measuring the concentrations of all species simultaneously at a single time is very difficult and therefore estimating the rate of reaction at any single time is very difficult.

<sup>2</sup>A complex reaction is one that involves more than one step. It is in direct contrast to an elementary reaction.



### 9.0.1 Mechanism vs. Molecularity vs. Reaction Order

A useful illustration of the distinctions between mechanism, molecularity, and reaction order comes from the analysis of *intramolecular* versions of typically *intermolecular* reactions. Consider the SN2 reaction between an alkyl iodide and an amine. The reaction is second-order overall, first-order in both the amine and alkyl iodide, and bimolecular (hence the “2” in SN2). The intermolecular reaction involves a backside attack of the nucleophilic amine on the halogenated carbon, displacing the iodide in a single step (Reaction I in Figure 9.2). This reaction will be second-order, with rate law

$$\text{rate} = k[\text{Amine}][\text{Alkyl Iodide}]$$

Now, consider the a long chain molecule that terminates on one end with an amine and on the other an iodide. Two types of SN2 reactions are possible: If two *different* molecules react (Reaction III), we still have the intermolecular reaction described above, and the product of the reaction would ultimately be a polymer (Reaction IV). Alternatively, an *intramolecular* reaction could occur in which the amine at one terminus of the molecule interacts with the iodide at the other terminus, producing a cyclic product (Reaction II).

The differing kinetic orders of these two reactions provides a simple means to select one product over the other. The polymerization reaction depends on the square of the concentration of the reactant from reaction III, whereas the cyclization is first-order with respect to the same reactant. Thus, we can mathematically show what we intuitively know to be true: High concentrations of disubstituted reactant will favor polymerization whereas low concentrations will favor cyclization. How can we determine at what concentration the favorability of either reaction changes?

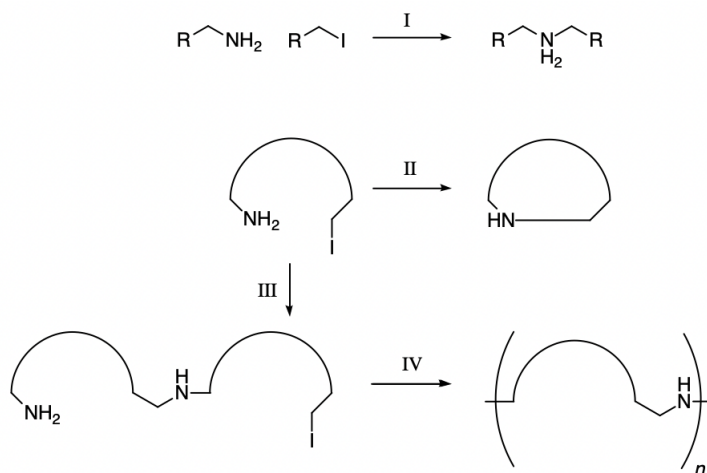


Figure 9.2: The difference between an intramolecular and intermolecular SN2 reaction.

In the scheme above, polymerization will be favored when reaction III occurs *faster* than reaction II, that is, when the ratio of their rate constants is greater than one. The ratio of these rate constants has units of molarity and is a characteristic of the particular system, known as the *effective molarity* (EM), defined as<sup>3</sup>

$$\text{EM} = \frac{k_{\text{intra}}}{k_{\text{inter}}} \quad (9.0.3)$$

Intuitively, the ratio of  $k_{\text{intra}}/k_{\text{inter}}$  should make sense (as opposed to  $k_{\text{inter}}/k_{\text{intra}}$ ) because the first-order rate constant,  $k_{\text{intra}}$ , has units  $\text{s}^{-1}$  whereas the second-order rate constant,  $k_{\text{inter}}$ , has units  $\text{M}^{-1} \text{s}^{-1}$  so that  $k_{\text{inter}}$  should always be in the denominator to achieve the proper units for EM.

<sup>3</sup>Note that this definition is more precisely known as the *kinetic effective molarity*. A *thermodynamic effective molarity* may also be defined as a ratio of equilibrium constants, however, we'll come to see that these ratios are equivalent by definition.

Now, we consider their ratios. For brevity, allow  $i$  to represent the disubstituted reactant in consideration:

$$\begin{aligned}\text{Rate of Reaction II: } \frac{d[i]}{dt} &= k_{intra}[i] \\ \text{Rate of Reaction III: } \frac{d[i]}{dt} &= k_{inter}[i]^2 \\ \text{Reaction III/Reaction II: } \frac{k_{inter}[i]^2}{k_{intra}[i]} &= \frac{k_{inter}}{k_{intra}}[i] = \frac{[i]}{EM}\end{aligned}$$

Thus, we see that when  $[i] > EM$ , the polymerized product will be favored over the cyclized product. Conversely, when  $[i] < EM$ , cyclization will occur more readily.

## The Spatial Temporal Postulate

The *spatial temporal postulate* posits that “the rate of reaction between moieties A and B is proportional to the time that A and B reside within a critical distance of one another.” Stated in words that actually make sense, the likelihood of a reaction occurring depends on how close and how long two functional groups come together. As a consequence, many *intramolecular reactions* are often faster than their *intermolecular* counterparts.

Within this postulate, the intuitive notion that time and space are critical factors for a reaction to occur are on display. Consider reaction I in Figure 9.2, in which an SN2 reaction is undergone between an amine and a halogenated alkane. The longer the amine and halogenated carbon spend close to one another with the correct geometry, the more likely the nucleophilic attack is to happen.

This postulate is oftentimes used to explain catalytic mechanisms where the distance between a catalyst and substrate determines binding, and the rate at which the catalyst can transform a substrate to product determines its catalytic efficiency.

## 9.1 First-Order Processes

A first-order process is one which has a rate law  $\text{rate} = k[A]$  for some reactant A. As we’ve seen in Equation (9.0.1), the rate law can be equivalently expressed as a differential equation of the form

$$\text{rate} = -\frac{d[A]}{dt} = k[A]$$

which can be solved using separation of variables:

$$\begin{aligned}-\frac{d[A]}{dt} &= k[A] \\ \int_{[A]_0}^{[A]_f} \frac{d[A]}{[A]} &= -\int_0^t k dt \\ \ln[A]_f &= -kt + \ln[A]_0 \\ [A]_f &= [A]_0 e^{-kt}\end{aligned}$$

Oftentimes this equation is rewritten using a *time constant*, defined as  $\tau = 1/k$ , affording

$$[A] = [A]_0 e^{-t/\tau} \quad (9.1.1)$$

which is the *integrated rate law for a first-order process*. The time constant has plenty of utility, the first of which is immediately recognizable because it has units of seconds, as opposed to the rate constant which has units of  $s^{-1}$  for a first-order reaction. With the integrated rate law we can determine the *half-life* of a substance, defined as the time it takes for exactly 50% of a substance to decay/transform/disappear etc. At this time,

$[A] = \frac{1}{2}[A]_0$  so that

$$\begin{aligned}\frac{1}{2}[A]_0 &= [A]_0 e^{-kt_{1/2}} \\ \frac{1}{2} &= e^{-kt_{1/2}} \\ \ln\left(\frac{1}{2}\right) &= -kt_{1/2} \\ t_{1/2} &= \frac{\ln 2}{k} = \tau \ln 2\end{aligned}\tag{9.1.2}$$

It is important to keep in mind that the half-life of a substance is always shorter than the time constant (consider the expression for  $t_{1/2}$  in terms of  $\tau$  in Equation (9.1.2) to convince yourself this is true). The half-life is the time it takes for a substance to decay to half of the concentration it was initially and the time constant is the time it takes for the substance to decay to  $1/e \approx 36.8\%$  of what it was initially.

A common misconception about the half-life of a chemical is that at  $t_{1/2}$ , half of the molecules in a substance suddenly react and disappear. Instead, it's actually the case that *the most amount of a substance's decay happens within the first few moments of a transformation*. Consider a graph of the integrated rate law for a first order reaction:

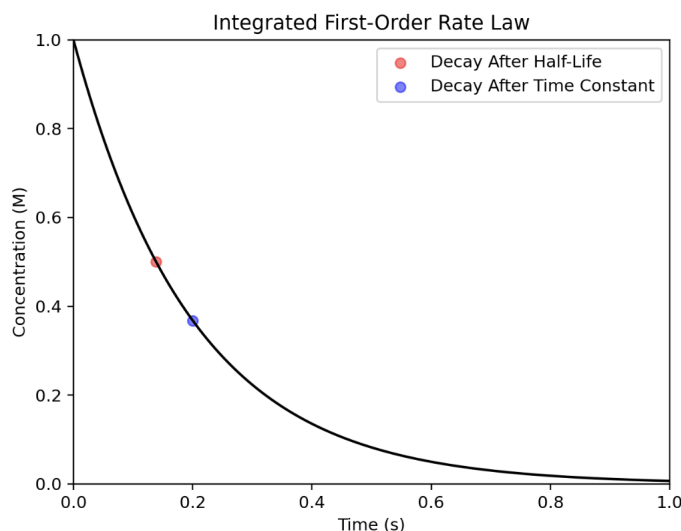


Figure 9.3: Exponential decay for a first-order reaction with  $k = 5 \text{ s}^{-1}$  and initial concentration  $[A]_0 = 1 \text{ M}$ .

It might be that the “continuous” nature of concentration that we illustrate in Figure 9.3 is obscuring our intuition. After all, molecules of A are transformed *discreetly* into product, not continuously, as if  $1/3$  of A can be transformed while leaving alone the remaining  $2/3$ . Our motivation to “discretize” the rate of decay of a chemical may be made easier with a *Poisson point process*, or just *Poisson process*.

I’ll preface the succeeding paragraph by saying I talk more than I probably should about probability. So, if you’re not uber familiar with some of the notation it might be confusing. Not to fear, however, because everything regarding the Poisson process is to bolster our understanding of first-order reactions.

Recall the *Poisson distribution*, a discrete probability distribution with rate parameter  $\lambda$ , defined on the nonnegative integers:

$$P(x) = \frac{e^{-\lambda} \lambda^x}{x!}, \quad x \in \{0, 1, 2, \dots\}$$

The random variable  $X$  counts the number of events that occurs in a given amount of exposure time, according to the rate  $\lambda$ . Using our definitions regarding rate laws above, if we allow  $n$  to be the number of times a chemical decays over the course of a fixed interval of time  $\theta$ , the rate of decay becomes  $\lambda = k\theta$  and we can

model the decay using a Poisson distribution:

$$P(n) = \frac{e^{-k\theta} (k\theta)^n}{n!}$$

The Poisson process models this sort of chemical transformation *very well* for numerous reasons. Firstly, the *sum of two Poisson distributions is another Poisson distribution*.<sup>4</sup> Using this fact, consider two random variables which model the amount of decay for the same substance A. Let  $X$  count the decay at a time  $t$  and let  $Y$  count the decay at a time  $t + T$ . Then, if we let  $S = Y - X$  be the difference in decay between the two states  $X$  and  $Y$ , we have that

$$P(S = n) = \frac{e^{-kT} (kT)^n}{n!}$$

which implies *the decay on the interval  $t + T$  is independent of the decay that happens on the interval of time immediately before*. This result is connected to the *memoryless property* of the Poisson distribution which says that the distribution of points over a finite interval does not affect the distribution of points on any other finite interval for a Poisson process. Intuitively, this result should make sense for the transformation of a chemical: For a first-order reaction in which the rate law is dependent on a single species A, why would the rate *law* change as the concentration of A changes? Obviously it wouldn't, and the Poisson process agrees with this intuition.

Okay last thing I'll mention about the Poisson process: A Poisson distribution can be thought of as a *limit of binomial distributions*.<sup>5</sup> If we consider each point on the curve of Figure 9.3 separately, we can imagine that at each infinitesimally small interval of time  $dt$  that a molecule of A has two options, either to decay or not to decay. This is exactly a binomial! Think of flipping a coin except one side is life and the other is death. In theory, we could model chemical decay using a binomial, I suppose, but the Poisson distribution is a better choice because it does this intrinsically while also incorporating a rate parameter, something that we've seen (and could have already intuited) is immensely important to the study of chemical kinetics.

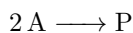
## 9.2 Second-Order Processes

A second-order reaction is just like a first-order reaction, except second-order. The principle difference in the case of a second-order reaction is that we have two types, one consisting of a reaction between a single species and itself and the other consisting of a reaction between two unique species.

As we'll come to see, the integrated rate laws for second-order processes (and  $n$ th-order processes for that matter) *depend on the initial concentrations of the reacting species*. Intuitively, this should make sense: In contrast to the first-order, unimolecular case, where we can think of a reactant just sort of "waiting" to react and is independent of the concentrations of any other species in solution, in the second-order, bimolecular case, the rate is dependent on how much of each reactant is present because two molecules are required for the reaction to proceed.

### 9.2.1 Type I Second-Order Processes

A *type I second-order process*, as it will be referred to, is a reaction of the form



<sup>4</sup>The proof of this isn't difficult but it involves some concepts in probability that I am not willing to write here and explain. So, if you want to know more you can either ask me or just look it up yourself.

<sup>5</sup>Another thing that has a relatively simple proof, but not one that is important enough for me to elaborate on here.

with a corresponding rate law

$$\text{rate} = \frac{d[\text{P}]}{dt} = -\frac{1}{2} \frac{d[\text{A}]}{dt} = k[\text{A}]^2 \quad (9.2.1)$$

This reaction will be “type I” because it is defined by only a single species. Notably, second-order reactions have what can be thought of as a “critical concentration,” in which the rate of reaction slows down or speeds up appreciably. In the scheme above, this is achieved at  $[\text{A}] = 1 \text{ M}$ . The rationale behind this comes from the power of 2 in the expression for the rate law and is also somewhat mentioned in the discussion on effective molarity in Section 9.0.1.

By Equation (9.2.1) we have the relationship

$$-\frac{d[\text{A}]}{dt} = 2k[\text{A}]^2$$

and so oftentimes we’ll refer to the *effective rate constant*,  $k_f = 2k$ . Determining the integrated rate law from this expression isn’t too hard:

$$\begin{aligned} -\frac{d[\text{A}]}{dt} &= k_f[\text{A}]^2 \\ -\int_{[\text{A}]_0}^{[\text{A}]} \frac{d[\text{A}]}{[\text{A}]^2} &= \int_0^t k_f dt \\ \frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} &= k_f t \\ \frac{1}{[\text{A}]} &= \frac{1}{[\text{A}]_0} + k_f t \end{aligned} \quad (9.2.2)$$

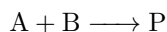
We can use Equation (9.2.2) to determine the half-life for a type I second-order process:

$$\begin{aligned} \frac{1}{\frac{1}{2}[\text{A}]_0} &= \frac{1}{[\text{A}]_0} + k_f t_{1/2} \\ t_{1/2} &= \frac{1}{k_f[\text{A}]_0} \end{aligned} \quad (9.2.3)$$

The inverse proportionality between  $t_{1/2}$  and the initial concentration of the single reacting species is indicative of the concentration dependence for processes of order  $> 1$ . Unlike the first-order unimolecular processes which we can think of as happening at a fixed rate regardless of the concentration, in order for a second-order, bimolecular reaction *to occur*, the reacting species must collide. Hence, a larger concentration of reacting species affords collisions which happen more often and therefore a faster rate.

### 9.2.2 Type II Second-Order Processes

A *type II second-order process*, as it will be referred to, is a reaction of the form



with a corresponding rate law

$$\text{rate} = \frac{d[\text{P}]}{dt} = -\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = k[\text{A}][\text{B}] \quad (9.2.4)$$

As we can see above, the rates of consumption for A and B are equal so that we can derive the relationship

$$\begin{aligned}\Delta[A] &= \Delta[B] \\ [A]_0 - [A] &= [B]_0 - [B] \\ [B]_0 - [A]_0 + [A] &= [B] \\ \Delta + [A] &= [B]\end{aligned}\tag{9.2.5}$$

where  $\Delta = [B]_0 - [A]_0$  is defined to simplify some expressions to come. With this definition, however, we're left to discover the integrated rate law for two cases, where  $\Delta = 0$  or  $\Delta \neq 0$ . Also, note that the  $\Delta$  used in the first line is to denote a change in concentration and has a different meaning than  $\Delta$  in the expression  $\Delta = [B]_0 - [A]_0$ . Substituting Equation (9.2.5) into (9.2.4) affords an expression which can be integrated to derive an expression for the concentration of reactants as a function of time:

$$\begin{aligned}-\frac{d[A]}{dt} &= k[A][B] \\ &= k[A](\Delta + [A]) \\ \int_{[A]_0}^{[A]} \frac{d[A]}{[A](\Delta + [A])} &= -\int_0^t k dt\end{aligned}\tag{9.2.6}$$

The above integral is not exactly trivial, and you could just look it up in the textbook or on google, but where's the fun in that? Instead, we'll evaluate it using fractional decomposition. First, suppose that we can rewrite

$$\frac{1}{[A](\Delta + [A])} = \frac{\alpha}{[A]} + \frac{\beta}{\Delta + [A]}\tag{9.2.7}$$

where  $\alpha$  and  $\beta$  are some constants to be determined. Cross-multiplying affords the relation

$$\begin{aligned}1 &= \alpha(\Delta + [A]) + \beta([A]) \\ &= \alpha\Delta + [A](\alpha + \beta)\end{aligned}\tag{9.2.8}$$

Here, notice that  $\Delta$  *is a constant*. It depends on the initial concentrations of each species A and B, however, these concentrations are fixed. In contrast,  $[A]$  is dependent on time and *is a variable*. The left-hand side of Equation (9.2.8) is purely constant so that we can rewrite

$$\begin{aligned}1 = \alpha\Delta &\Rightarrow \alpha = \frac{1}{\Delta} \\ 0 = [A](\alpha + \beta) &\Rightarrow \alpha = -\beta\end{aligned}$$

Thus, Equation (9.2.7) can be rewritten as

$$\frac{1}{[A](\Delta + [A])} = \frac{1}{\Delta[A]} - \frac{1}{\Delta(\Delta + [A])}$$

and substituted into (9.2.6) to assist integration:

$$\begin{aligned}
 \int_{[A]_0}^{[A]} \left( \frac{1}{\Delta[A]} - \frac{1}{\Delta(\Delta + [A])} \right) d[A] &= - \int_0^t k dt \\
 \int_{[A]_0}^{[A]} \frac{d[A]}{\Delta[A]} - \int_{[A]_0}^{[A]} \frac{d[A]}{\Delta(\Delta + [A])} &= -kt \\
 \frac{1}{\Delta} \left[ \ln([A]) - \ln(\Delta + [A]) \right]_{[A]_0}^{[A]} &= -kt \\
 -\frac{1}{\Delta} \left[ \ln\left(\frac{[A]}{\Delta + [A]}\right) - \ln\left(\frac{[A]_0}{\Delta + [A]_0}\right) \right] &= kt \\
 -\frac{1}{\Delta} \left[ \ln\left(\frac{[A]}{[B]}\right) - \ln\left(\frac{[A]_0}{[B]_0}\right) \right] &= kt \\
 \frac{1}{\Delta} \left[ \ln\left(\frac{[B]}{[A]}\right) - \ln\left(\frac{[B]_0}{[A]_0}\right) \right] &= kt \\
 \frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) &= kt
 \end{aligned} \tag{9.2.9}$$

Equation (9.2.9) is the *integrated rate law for a type II second-order reaction*. Recall, however, that our expression for  $\Delta$  held only when  $[B]_0 \neq [A]_0$  and therefore this expression is valid only when  $\Delta \neq 0$ . In the case where  $[B]_0 = [A]_0$ , the concentrations of  $[A]$  and  $[B]$  reduce to the expression for a type I second-order reaction with  $k = k_f$  in Equation (9.2.2).

Finally, the idea of a half-life does not apply to reactions of this type. Unless the reactants are mixed in stoichiometric proportion (for the reaction discussed in this section that would be 1:1), the concentrations of the reacting species will not be half of their initial concentrations at identical times.

### 9.3 Nth-Order Processes of a Single Component

The principles governing the rate of an  $n$ th-order reaction of a single species are very similar to those of a first-order reaction, aside from the order of reaction. In general, we could model the rate of reaction for this sort of process as

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^n \tag{9.3.1}$$

for any integer  $n > 1$ . This can be solved in a similar manner to the corresponding equation for a first-order process, using separation of variables:

$$\begin{aligned}
 -\frac{d[A]}{dt} &= k[A]^n \\
 \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^n} &= - \int_0^t k dt \\
 -\frac{1}{n-1} \left( \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) &= -kt \\
 \frac{1}{[A]^{n-1}} &= (n-1)kt + \frac{1}{[A]_0^{n-1}}
 \end{aligned} \tag{9.3.2}$$

Equation (9.3.2) is the integrated rate law for an  $n$ th-order process. The half-life for an  $n$ th-order reaction can be found just as we did in the first-order case by allowing  $[A] = \frac{1}{2}[A]_0$ :

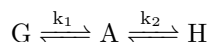
$$\begin{aligned}\frac{1}{\left(\frac{1}{2}[A]_0\right)^{n-1}} &= (n-1)kt_{1/2} + \frac{1}{[A]_0^{n-1}} \\ \frac{2^{n-1} - 1}{[A]_0^{n-1}} &= (n-1)kt_{1/2} \\ t_{1/2} &= \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}\end{aligned}\tag{9.3.3}$$

Notably, the half-life for an  $n$ th-order process *depends on the initial concentration*. Because of this, the concept of a half-life becomes far less useful for reactions which aren't first-order.

## 9.4 Parallel Pathways

### Iodine Clock

We now turn our attention to reactions of the form,



where a single reactant A may react to form either of two products, G or H. The set of rate equations for this sort of transformation may be modeled as

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] - k_2[A] = -(k_1 + k_2)[A] \\ \frac{d[G]}{dt} &= k_1[A] \\ \frac{d[H]}{dt} &= k_2[A]\end{aligned}$$

We can solve for the concentration of A as a function of time first, and then substitute this expression into the differential equations for G and H to solve for their time-dependent concentration as well. Solving for [A] as a function of time,

$$\begin{aligned}\frac{d[A]}{dt} &= -(k_1 + k_2)[A] \\ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} &= \int_0^t -(k_1 + k_2)dt \\ \ln [A] - \ln [A]_0 &= -(k_1 + k_2)t \\ [A] &= [A]_0 e^{-(k_1 + k_2)t}\end{aligned}\tag{9.4.1}$$

Equation (9.4.1) is the integrated rate law of a parallel pathway reaction. Since the rate constants  $k_1$  and  $k_2$  are restricted positive, the rate of decay of A will *always* be greater in a parallel pathway reaction than in the first-order reaction of A to either of the two products. Intuitively, this makes sense because in this reaction scheme there are more ways for A to be transformed than there are in just a normal first-order reaction.



Now we can find expressions for  $[G]$  and  $[H]$  as a function of time. First,  $[G]$ :

$$\begin{aligned}\frac{d[G]}{dt} &= k_1[A] \\ \frac{d[G]}{dt} &= k_1[A]_0 e^{-(k_1+k_2)t} \\ \int_{[G]_0}^{[G]} d[G] &= \int_0^t k_1[A]_0 e^{-(k_1+k_2)t} dt \\ [G] - [G]_0 &= k_1[A]_0 \left[ \frac{-1}{k_1+k_2} e^{-(k_1+k_2)t} \right]_0^t \\ [G] &= \frac{k_1[A]_0}{k_1+k_2} \left( 1 - e^{-(k_1+k_2)t} \right) + [G]_0\end{aligned}$$

Notice that in the limit that  $k_2 \rightarrow 0$ , that is, when the reaction  $A \longrightarrow H$  stops happening, all of  $[A]_0$  eventually becomes  $G$ . This is sort of like a check to make sure our expression is correct. Hopefully unsurprisingly, we can derive a similar expression for  $[H]$ ,

$$[H] = \frac{k_2[A]_0}{k_1+k_2} \left( 1 - e^{-(k_1+k_2)t} \right) + [H]_0$$

and in the limit as  $k_1 \rightarrow 0$  we see a similar result.

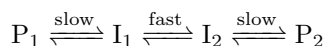
The key result that can be seen between these two expressions is that the fraction of  $A$  that is transformed into either  $G$  or  $H$  depends on how quickly  $G$  and  $H$  are made relative to one another. This was indirectly implied when referring to the final concentrations of product in the limit as one of the rate constants went to zero. If we instead consider concentration of product in the limit that time is allowed to tend to infinity, we find that

$$\frac{[G]_\infty}{[H]_\infty} = \lim_{t \rightarrow \infty} \left( \frac{\frac{k_1[A]_0}{k_1+k_2} (1 - e^{-(k_1+k_2)t})}{\frac{k_2[A]_0}{k_1+k_2} (1 - e^{-(k_1+k_2)t})} \right) = \frac{k_1}{k_2} \quad (9.4.2)$$

Thus, we find that the ratio of products when the parallel pathway reaction is allowed to go to completion is dependent on how quickly the products are created relative to one another. Equation (9.4.2) affords a results very different from what we would expect from thermodynamics which would insist that the product which prevails at equilibrium is the one with the lowest free energy, not necessarily the one which is formed more rapidly. However, this result makes more sense when we consider the fact that no sort of reversibility among the reactants and products was allowed, implying that even though  $G$  may have a lower free energy than  $H$ , for example,  $G$  cannot react to form  $H$  in any way.

### 9.4.1 The Curtin-Hammett Principle

The Curtin-Hammett principle is concerned with product ratios for a parallel pathway reaction scheme of the form



where the activation energy for the interconversion of  $I_1$  and  $I_2$  is far less than either of the activation energies for the formation of product. Then, the principle states that the ratio of the products is determined by the relative heights of the highest energy barriers leading to the different products and is not significantly influenced by the relative energies of the isomers, conformers, or intermediates formed prior to the highest energy transition states.

In Figure 9.4 we have a reaction in which a pair of intermediates,  $I_1$  and  $I_2$ , can readily equilibrate because their activation energies to form either of  $P_1$  or  $P_2$  is much higher. By the Curtin-Hammett principle, since the activation energy to go from  $I_1$  to  $P_1$  is less than that of the competing reaction, the major product in Figure 9.4 will be  $P_1$ .

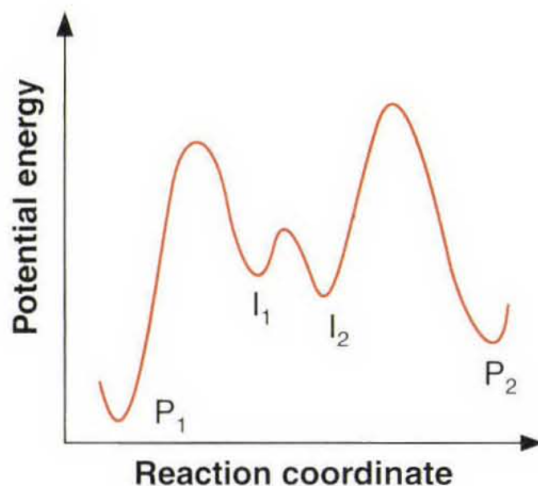


Figure 9.4: Reaction coordinate diagram demonstrating the Curtin-Hammett principle.

This principle has highly beneficial implications in all sorts of areas. The reason I know about this principle is because of the following question: We all know and love the Wittig reaction from Orgo 2, but the “brother” reaction, the *Horner-Wadsworth-Emmons (HWE) reaction*, hosts as much if not more utility. The major contrast between the two couplings is the stereochemistry of the products. While the Wittig reaction utilizes a phosphonium ylide to convert carbonyls to Z-alkenes, the HWE reaction uses a phosphonate carbanion to produce the E-alkene.

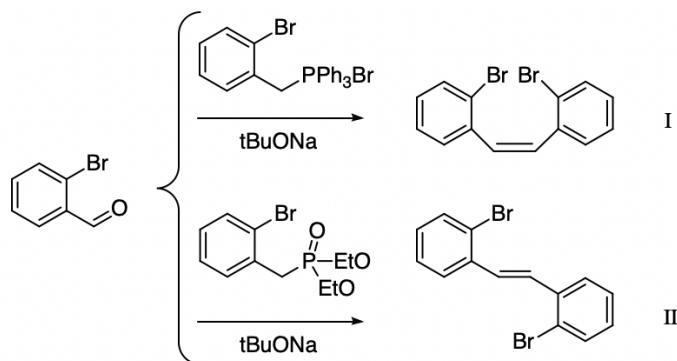


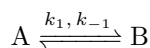
Figure 9.5: The Wittig product, I, in contrast with the HWE product, II. The only difference comes from the type of reagent being used which has an effect on the energy of the transition state for each reaction.

The difference between which is the major isomer for these reactions can be explained using the mechanisms for either of these reactions and the Curtin-Hammett principle. Obviously I *could* explain it if I wanted to, but it’s beyond the scope of this course so I’ll spare you the details.

## 9.5 Reversible Reactions

Near the end of Section 9.4, the contrasting results between kinetics and thermodynamics we arrive at for a reaction which is allowed to reach equilibrium is semi-explained on the basis of irreversibility between reactants and products. Now, we’ll consider a reversible reaction and come to see that the kinetic result agrees with our thermodynamic intuition.

Consider a reversible reaction



with forward rate constant  $k_1$  and reverse rate constant  $k_{-1}$ . The rate of formation for A and B can be modeled as usual by

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] + k_{-1}[B] \\ \frac{d[B]}{dt} &= k_1[A] - k_{-1}[B]\end{aligned}$$

At equilibrium, we'd expect that the concentrations of each species will stop changing, that is,  $d[A]/dt = d[B]/dt = 0$ . Then, using either of the two rate equations we have that  $k_1[A]_{\text{eq}} = k_{-1}[B]_{\text{eq}}$  and therefore

$$\frac{[B]_{\text{eq}}}{[A]_{\text{eq}}} = \frac{k_1}{k_{-1}} = K_{eq} \quad (9.5.1)$$

This equation is known as *detailed balance*, and it connects the mathematical results from kinetics to our thermodynamic intuition. More formally, it tells us that at equilibrium, each elementary process within a set of reactions is in equilibrium with its reverse process and that the equilibrium constant may be expressed in terms of rate constants.

Most formally, the principle of detailed balance states that at equilibrium, the forward rate of each step is equal to the reverse rate of that step. It's been recognized and proven in both classical mechanics and quantum mechanics the principle of microscopic reversibility, that is, the equations of mechanics are *time-reversal invariant*. This implies that for every possible type of interaction between particles the exact reverse is also possible.

Detailed balance also allows us to make explicit appeals to thermodynamics. If B is more stable than A and therefore  $K_{eq} > 1$ , the formation B will occur faster than the formation of A.

As far as the behavior of a reaction away from equilibrium goes, we turn back to the language of differential equations. By the conservation of mass, we have that  $[B] = [A]_0 - [A]$  (or, equivalently,  $[A] = [B]_0 - [B]$ . Here we'll assume that  $[B]_0 = 0$  so the former equation for  $[B]$  will be used) which allows us to solve the expression for  $d[A]/dt$  and express  $[A]$  as a function of time:

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] + k_{-1}([A]_0 - [A]) \\ &= -k_1[A] + k_{-1}([A]_0 - [A]) \\ [\dot{A}] + (k_1 + k_{-1})[A] &= k_{-1}[A]_0\end{aligned} \quad (9.5.2)$$

<sup>6</sup>The solution to this differential equation isn't quite trivial, so I'm gonna provide the solution: This equation is classified as a *first-order, linear ordinary differential equation* and can be solved using an *integrating factor*. For the expression above, the integrating factor is defined as

$$e^{\int (k_1 + k_{-1}) dt} = e^{(k_1 + k_{-1})t}$$

and when Equation (9.5.2) is multiplied through by this factor, a nice simplification is afforded by the product

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<sup>6</sup>Note that in Equation (9.5.2) I used the notation  $[\dot{A}]$  to express the derivative of  $[A]$  with respect to time. In general, this notation *always* refers to a derivative with respect to time.

rule:

$$\begin{aligned}
 e^{(k_1+k_{-1})t}[\dot{A}] + e^{(k_1+k_{-1})t}(k_1 + k_{-1})[A] &= e^{(k_1+k_{-1})t}k_{-1}[A]_0 \\
 \frac{d}{dt} \left[ e^{(k_1+k_{-1})t}[A] \right] &= e^{(k_1+k_{-1})t}k_{-1}[A]_0 \\
 e^{(k_1+k_{-1})t}[A] &= \int k_{-1}[A]_0 e^{(k_1+k_{-1})t} dt \\
 e^{(k_1+k_{-1})t}[A] &= \frac{k_{-1}[A]_0}{k_1 + k_{-1}} e^{(k_1+k_{-1})t} + C \\
 [A] &= \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + C e^{-(k_1+k_{-1})t} \tag{9.5.3}
 \end{aligned}$$

In the second line of the sequence above, the product rule was invoked “backward” to allow simple integration by the fundamental theorem of calculus. Equation (9.5.3) is nearly our final answer, except for the constant  $C$ . To evaluate the constant in terms of physical characteristics of the system we can use the condition that at time  $t = 0$ , the concentration of A must be  $[A] = [A]_0$ . Then,

$$\begin{aligned}
 [A]_0 &= \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + C e^{-(k_1+k_{-1})(0)} \\
 C &= [A]_0 - \frac{k_{-1}[A]_0}{k_1 + k_{-1}} \\
 C &= [A]_0 \left( \frac{k_1}{k_1 + k_{-1}} \right)
 \end{aligned}$$

Plugging this result back into Equation (9.5.3) affords our final result for the concentration of [A] as a function of time:

$$[A] = [A]_0 \left( \frac{k_1 e^{-(k_1+k_{-1})t} + k_{-1}}{k_1 + k_{-1}} \right) \tag{9.5.4}$$

While at first glance it may look complicated, Equation (9.5.3) is still a simple exponential decay with time constant  $\tau = 1/(k_1 + k_{-1})$ . In contrast to previous examples, however, in the limit as  $t \rightarrow \infty$  the concentration of [A] remains nonzero since the reaction is reversible.

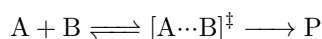
## 9.6 Transition State Theory

*Transition state theory (TST)* is directed toward the calculation of rate constants at equilibrium. Inspired by thermodynamics, TST explains the rates of elementary reactions under the assumption that the activated complexes of a transition state are in quasi-equilibrium with the reactants. Then, the rate of reaction is directly proportional to the concentration of these complexes multiplied by some frequency with which they are converted to products.

The basic ideas of TST can be summarized as follows:

1. Rates of reaction can be studied by examining activated complexes near the transition state.
2. The activated complexes are in *quasi-equilibrium* with the reactant molecules.
3. The activated complexes can convert into products, and kinetic theory can be used to calculate the rate of this conversion.

Arguably the most important feature of this theory is the notion that reactants can be thought of as in equilibrium with the transition state complex as opposed to being in equilibrium with the product. This idea affords a reaction scheme of the type



where  $AB^\ddagger$  represents the transition state the reaction passes through. This model begs the question, what is the probability of being in the transition state? Or, how can we estimate the “equilibrium” concentrations of reactants and the transition state complex? We’ll start by defining a new quantity, the equilibrium constant for the reaction between the reactants and transition state:

$$\frac{[A\cdots B]^\ddagger}{[A][B]} = K_\ddagger = e^{-\Delta G^\ddagger/RT} \quad (9.6.1)$$

$\Delta G^\ddagger$  is the free energy change going from the reactants to the transition state and will be positive by the nature of the instability of the transition state complex. This is a good start to characterizing the energy associated with the transition state complex, however, it’s not a rate!

To go about solving for the quantity we care about, the rate constant, we turn to Eyring, Evans, and Polanyi (all really smart scientists) who illustrated that the rate of a reaction is directly proportional to some frequency factor with which the transition state complexes are converted to products. I mentioned it only a few moments ago but I’ll do it again just because it’s the basis on which TST is founded, the notion that the rate constant can be determined this way relies on the fact that there is a quasi-equilibrium between reactants and the transition state complex.

The most basic assumption is that bonds of a reactant act like a harmonic oscillator, such that their energies can be modeled as  $U = \frac{1}{2}kx^2$  where  $U$  is the potential energy stored in the bond,  $k$  is some proportionality constant, and  $x$  is the bond length. From classical mechanics we have the result that the angular momentum of the oscillator  $\omega$  is given by  $\omega = \sqrt{k/\mu}$  where  $\mu$  acts as the “reduced mass” of the bond. While this information is all helpful, it won’t be of great use in trying to find the rate constant for the reaction between the reactants and the transition state complex.

To make our lives harder/more fun, quantum mechanics tells us that the ground state energy of a harmonic oscillator must be *at least*

$$E = \frac{(\Delta p)^2}{2m} + \frac{1}{2}m(\omega\Delta x)^2$$

which is a sum of the kinetic and potential energies, and the uncertainty principle is invoked for the position and momentum of the particle. Recall that the Heisenberg uncertainty principle formally states that  $\Delta x\Delta p \geq \hbar/2$ . Taking the lower limit of this inequality (that is, making it an equality), we’re left with

$$E = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}m(\omega\Delta x)^2 \quad (9.6.2)$$

and by differentiating the energy with respect to the uncertainty in position we can find the value of  $\Delta x$  such that the energy will be minimized, i.e., the energy of the ground state:

$$\begin{aligned} \frac{\partial E}{\partial \Delta x} &= \frac{\partial}{\partial \Delta x} \left[ \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}m(\omega\Delta x)^2 \right] \\ 0 &= -\frac{\hbar^2}{4m(\Delta x)^3} + m\omega^2\Delta x \\ \frac{\hbar^2}{4m(\Delta x)^3} &= m\omega^2\Delta x \\ \Delta x &= \sqrt{\frac{\hbar}{2m\omega}} \end{aligned}$$

Substituting this result back into Equation (9.6.2) affords the ground state energy of a harmonic oscillator:

$$\begin{aligned} E_{gs} &= \frac{\hbar^2}{8m \left( \sqrt{\frac{\hbar}{2m\omega}} \right)^2} + \frac{1}{2} m \omega^2 \left( \sqrt{\frac{\hbar}{2m\omega}} \right)^2 \\ &= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} \\ &= \frac{\hbar\omega}{2} \end{aligned} \quad (9.6.3)$$

Why is that at all useful? I'm told it will be next semester. For now, though, it tells us that the ground state energy is simply  $E_{gs} = \frac{1}{2}\hbar\omega$ . In addition to this fact, recall from all the way back in Section 7.2.1 in our discussion of the microcanonical ensemble, Equation (7.2.13) tells us that the *average amount of kinetic energy carried per harmonic mode of an oscillator is  $k_B T/2$* . To think that Dr. Fried didn't even cover this derivation in class and yet it's come up time and time again in later lectures and even on some exams blows my mind, but that's besides the point. What is not besides the point, however, is the relationship we're left with:

$$\frac{\hbar\omega}{2} = \frac{k_B T}{2}$$

for the ground state energy of a single harmonic mode associated with this harmonic oscillator.<sup>7</sup> Before arriving at our desired result, recall that the linear frequency,  $\nu$ , of an oscillator is related to the angular frequency by the relationship  $\nu = 2\pi\omega$  (also illustrated in Figure 9.6) so that we're left with

$$\begin{aligned} \frac{\hbar\omega}{2} &= \frac{\hbar\nu}{4\pi} = \frac{k_B T}{2} \\ \frac{\hbar\nu}{2} &= \frac{k_B T}{2} \\ \nu &= \frac{k_B T}{h} \end{aligned} \quad (9.6.4)$$

Equation (9.6.4) (notice the units... it's in  $s^{-1}$ ) is the frequency factor associated with the transformation of the transition state complex into product, also known as Eyring's frequency factor.

Finally, we can write an expression for the rate constant associated with crossing of the activated energy barrier as

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT} \quad (9.6.5)$$

where  $k_B T/h$  is the frequency factor which describes the frequency with which molecules are vibrating about, weighted down by a Boltzmann factor which characterizes the probability that a particle will have sufficient energy to actually cross the activation energy barrier. This equation is also known as the *Eyring equation*. The benefit of the Eyring equation is that it allows us to calculate reaction rates based on thermodynamic properties of a system. In particular, by rearranging Equation (9.6.5) we can show that

$$\begin{aligned} \frac{kh}{k_B T} &= e^{-\Delta G^\ddagger/RT} \\ \ln \left( \frac{kh}{k_B T} \right) &= \frac{-\Delta G^\ddagger}{RT} \\ \ln \left( \frac{kh}{k_B T} \right) &= \left( \frac{-\Delta H^\ddagger}{R} \right) \frac{1}{T} + \frac{\Delta S^\ddagger}{R} \end{aligned} \quad (9.6.6)$$

<sup>7</sup>The "harmonic mode" refers to the frequency of the associated wave. Waves can have all sorts of frequencies! Some we can hear, and others we can't. What's important here is to recognize that waves associated with electrons and other particles are allowed to have only *certain* harmonic modes because their energies are quantized. Thus, when we refer to a "harmonic mode" we're referring to a particular quantum of energy associated with a wave. The ground state of a particle is one of these modes.

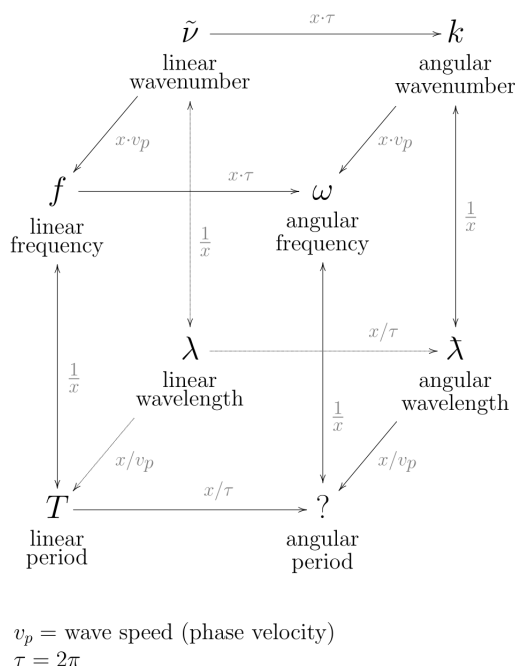


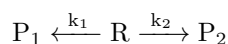
Figure 9.6: I’ve had this picture saved on my desktop for a while cause I think it’s pretty helpful. The one relationship that we did need between the linear and angular frequencies is on there, as well as many more that are not nearly as useful for us.

which is the *Eyring plot*, affording a graph of  $\ln(kh/k_B T)$  vs.  $1/T$  with a slope proportional to the *enthalpy of activation* and an intercept proportional to the *entropy of activation*. Notice the *immense* similarity of the Eyring plot to the van’t Hoff plot.

This equation is helpful because it tells us that the temperature dependence of a chemical reaction is a reflection of whether or not the transition state is enthalpically or entropically expensive to create. The entropic expense is related to how conformationally restricted the transition state is and the enthalpic expense comes from how much weaker/stronger the bonds of the transition state are or how much steric repulsion/hindrance is present.

During lecture Dr. Fried briefly discusses Arrhenius theory and how lame it is which is why I’ve opted to ignore it here as well. Notice that, in essence, we’re performing the same exact experiment as we would have using the Arrhenius model, however, using TST we’re gaining much more insight into the thermodynamics of the reaction.

Here’s a question regarding kinetics and transition state theory: Consider the following reaction scheme.



Suppose that at room temperature,  $k_1 = 1 \text{ s}^{-1}$  and  $k_2 = 4 \text{ s}^{-1}$ . Moreover, suppose that  $[R_0] = 1.0 \text{ M}$ . What are the concentrations of R,  $P_1$ , and  $P_2$  as  $t \rightarrow \infty$ ? Well, we could answer this question by writing out the rate laws and doing some calculus, similar to the derivation of Equation (9.4.1). However, I’ve already done this derivation (in Equation (9.4.1), obviously)! So instead we can argue that since these reactions *are not reversible* the ratio of products must followed detailed balance, such that

$$\frac{[P_1]}{[P_2]} = \frac{k_1}{k_2} = \frac{1}{4} = 0.25$$

Moreover, since neither reaction is reversible we know that all of the reactant will be converted to product as  $t \rightarrow \infty$  which allows us to work out that at equilibrium,  $[P]_1 = 0.2 \text{ M}$  and  $[P]_2 = 0.8 \text{ M}$ .

Now, suppose that we have a single molecule of the reactant R, and at  $t = 0$  it becomes “activated” so

that it is allowed to react. Sketch curves corresponding to the probability the R molecule still exists, and that  $P_1$ , after a given time, now exists. I did this here using Python to make it look sorta nice, using the parameters as they're described in the question.

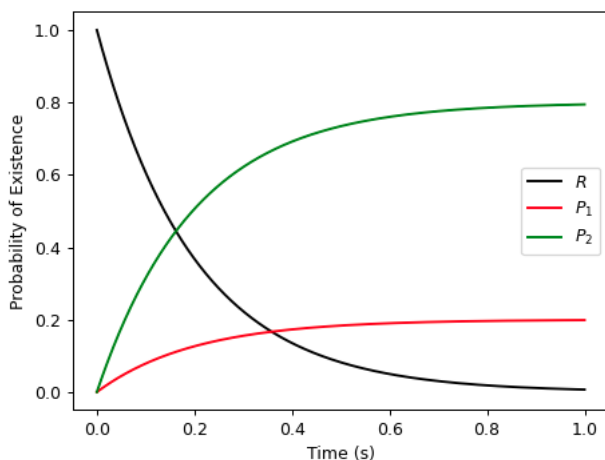


Figure 9.7: Probabilities of existence for each species in the reaction scheme.

The important aspects of Figure 9.7 are that the total waiting time  $\tau = 1/(k_1 + k_2)$  for R is 0.2 s so that after that amount of time, R has decayed to  $\frac{1}{e} \approx 36\%$  of its initial concentration. Similarly, make sure to note that in the graph for the probability of  $P_1$  existing, the plot begins at 0 and increases exponentially to 0.2, the maximal concentration at equilibrium.

These probabilities are nice and all, but we can paint a slightly more detailed picture of the thermodynamics of these reactions using transition state theory. So, using TST, derive an equation for the product ratio  $[P_1]/[P_2]$  as function of temperature and activation barriers,  $\Delta G^\ddagger$ . Again, we'll invoke detailed balance to do this. Moreover, we'll make use of Equation (9.6.5), the Eyring equation, to express the rate constants in terms of activation barriers:

$$\begin{aligned} \frac{[P_1]}{[P_2]} &= \frac{k_1}{k_2} = \frac{\frac{k_B T}{h} e^{-\Delta G_1^\ddagger/RT}}{\frac{k_B T}{h} e^{-\Delta G_2^\ddagger/RT}} \\ &= \exp \left\{ \frac{-(\Delta G_1^\ddagger - \Delta G_2^\ddagger)}{RT} \right\} \\ &= \exp \left\{ \frac{-\Delta \Delta G^\ddagger}{RT} \right\} \end{aligned}$$

Great! Now, suppose that  $P_2$  is a coveted molecule and so we're trying to design our synthesis in order to maximize the production of it. Further suppose we discover that increasing the temperature causes the selectivity of  $P_2$  to increase. Use TST to infer what this implies about the relative values of the transition state activation parameters,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , between the two reactions. To discover more about the parameters we'll turn to the Eyring equation again, in conjunction with detailed balance, this time substituting  $\Delta G^\ddagger$  for  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .

$$\begin{aligned} \frac{[P_1]}{[P_2]} &= \frac{\exp \left\{ \frac{-(\Delta H_1^\ddagger - T\Delta S_1^\ddagger)}{RT} \right\}}{\exp \left\{ \frac{-(\Delta H_2^\ddagger - T\Delta S_2^\ddagger)}{RT} \right\}} \\ &= \exp \left\{ \frac{-(\Delta H_1^\ddagger - \Delta H_2^\ddagger)}{RT} \right\} \exp \left\{ \frac{\Delta S_1^\ddagger - \Delta S_2^\ddagger}{R} \right\} \end{aligned}$$

Notice that in order for the selectivity of  $P_2$  to increase with temperature, we require that  $\Delta H_2^\ddagger > \Delta H_1^\ddagger$ . This



way, the exponential term containing the enthalpies gets smaller (in absolute value) with temperature and the product ratio  $[P]_1/[P]_2$  decreases. We've talked about this before, but whenever we consider the temperature effects on a reaction the enthalpy should come to mind. A greater enthalpy of activation would imply that the reaction is "more sensitive to temperature." This can also be rationalized using Le Chatelier's principle: if a reaction is highly exothermic, for example, then even a small increase in temperature will greatly shift the equilibrium distribution towards the reactants.

Now that's all fine and dandy, however, if we purport that  $\Delta H_2^\ddagger > \Delta H_1^\ddagger$  then that would imply reaction 2 were *slower* than reaction 1 under the initial conditions (using the Eyring equation to help guide our logic once again). Clearly, this contradicts the given information because we know that  $k_2 > k_1$ . Hence, the only way for reaction 2 to be faster than reaction 1 under these given conditions granted  $\Delta H_2^\ddagger > \Delta H_1^\ddagger$  is that  $\Delta S_2^\ddagger > \Delta S_1^\ddagger$  to begin with.

Finally, suppose that we run some experiments to acquire some data and find that  $\Delta S_2^\ddagger = -14 \text{ cal/mol/K}$ . Suppose that we also know that the standard entropy of the reactant R is  $S^\circ = 350 \text{ J/mol/K}$ . At room temperature, how many microstates are associated with  $TS_2$ , the transition state between R and  $P_2$ ? We can determine the number of microstates using Boltzmann's equation, however, we first need to find the entropy associated with the transition state. The entropy is given by

$$S^\ddagger = S^\circ + \Delta S^\ddagger$$

If you're having trouble visualizing this, trying drawing a reaction coordinate diagram. Making sure to convert units, we're left with

$$S^\ddagger = 350 \text{ J/mol/K} - 14 \text{ cal/mol/K}(4.184 \text{ J/cal}) = 291.42 \text{ J/mol/K}$$

Then, we can find the number of microstates associated with the transition state of  $P_2$  as

$$S_2^\ddagger = Nk_B \ln W_2$$

$$W_2 = \exp \left\{ \frac{291.42}{Nk_B} \right\} \approx 1.68 \times 10^{15}$$

Although we can calculate the transition state entropy at standard state conditions, what quantity would we need to know in order to see how  $S_2^\ddagger$  changes with temperature? To see this, recall the second law of thermodynamics which states

$$dS = \frac{dq}{T}$$

for a reversible reaction. With a little bit of calculus we can show that

$$S = \int_{T_0}^T \frac{dq}{T} = \int_{T_0}^T \frac{C_P dT}{T} = C_P \ln \left( \frac{T}{T_0} \right) + C$$

$$S(T) = S(T_0) + C_P \ln \left( \frac{T}{T_0} \right)$$

where  $C_P$  is the heat capacity of the material. Since everything involved in this equation is a state function, we have

$$\Delta S(T) = \Delta S(T_0) + \Delta C_P \ln \left( \frac{T}{T_0} \right)$$

which also holds for the transition state

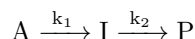
$$\Delta S^\ddagger(T) = \Delta S^\ddagger(T_0) + \Delta C_P^\ddagger \ln \left( \frac{T}{T_0} \right)$$

Thus, in order to determine how  $S_2^\ddagger$  changes with temperature we require the heat capacity of the transition state.

### 9.6.1 Hammond's Postulate

## 9.7 Consecutive Reactions

*Consecutive reactions*, or *sequential reactions*, occur through a series of steps of which reactants are transformed into intermediates, which in turn are transformed into product. The scheme for a consecutive reaction may look like



where A is a reactant, I is an intermediate, and P is the product. We can write rate laws for each step in the process as,

$$\frac{d[A]}{dt} = -k_1[A] \quad (9.7.1)$$

$$\frac{d[I]}{dt} = k_1[A] - k_2[I] \quad (9.7.2)$$

$$\frac{d[P]}{dt} = k_2[I] \quad (9.7.3)$$

which follow naturally from the elementary reaction steps in which a given species participates. To make solving a system of differential equations such as this possible, we'll begin by making two assumptions: Firstly, suppose that only A is present initially so that  $[I]_0 = [P]_0 = 0$  M. With this, the first reaction in the series simplifies to the case of a first-order reaction and the concentration of A as a function of time simplifies as Equation (9.1.1) to

$$[A] = [A]_0 e^{-k_1 t} \quad (9.7.4)$$

With this expression we can solve Equation (9.7.2) for the concentration of I as a function of time. Plugging in our new expression for [A],

$$\begin{aligned} \frac{d[I]}{dt} &= k_1[A]_0 e^{-k_1 t} - k_2[I] \\ \dot{[I]} + k_2[I] &= k_1[A]_0 e^{-k_1 t} \end{aligned} \quad (9.7.5)$$

In Section 9.5 we solved a similar sort of differential equation by the method of integrating factors. We'll take the same approach here. First notice that the integrating factor for this expression is given by

$$e^{\int k_2 dt} = e^{k_2 t}$$

and multiplying Equation (9.7.5) through by this factor affords

$$\begin{aligned} e^{k_2 t} \dot{[I]} + k_2 e^{k_2 t} [I] &= k_1 e^{k_2 t} [A]_0 e^{-k_1 t} \\ \frac{d}{dt} \left[ e^{k_2 t} [I] \right] &= k_1 [A]_0 e^{(k_2 - k_1)t} \\ e^{k_2 t} [I] &= \int_0^t k_1 [A]_0 e^{(k_2 - k_1)t} dt \\ e^{k_2 t} [I] &= \frac{k_1}{k_2 - k_1} [A]_0 e^{(k_2 - k_1)t} + C \\ [I] &= \frac{k_1}{k_2 - k_1} [A]_0 e^{-k_1 t} + C e^{-k_2 t} \end{aligned}$$

At  $t = 0$ ,  $[I]_0 = 0$  M and therefore

$$0 = \frac{k_1}{k_2 - k_1} [A]_0 + C$$

$$C = -\frac{k_1}{k_2 - k_1} [A]_0$$

so that we have an expression for the concentration of  $[I]$  as a function of time given by

$$[I] = \frac{k_1 [A]_0}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \quad (9.7.6)$$

Lastly, we can use Equations (9.7.4) and (9.7.6) to solve for the concentration of  $P$  as a function of time. First, notice that the concentration of all species at any time  $t$  must be no greater than the initial concentration of  $A$ <sup>8</sup> so that we're left with the relation

$$[A]_0 = [A] + [I] + [P]$$

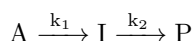
$$[P] = [A]_0 - [A] - [I]$$

Thankfully this isn't a differential equation so we won't need to do any cheeky integration. Instead, we can substitute our expressions for  $[A]$  and  $[I]$  directly:

$$[P] = [A]_0 \left( 1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right) \quad (9.7.7)$$

### Maximum Intermediate Species Concentration

For a reaction of the form,



we can use Equation (9.7.6) and the fact that for a maximum concentration it must be the case that  $d[I]/dt = 0$  to determine the time at which the maximum possible intermediate species concentration occurs:

$$\begin{aligned} \frac{d[I]}{dt} &= \frac{d}{dt} \left[ \frac{k_1 [A]_0}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) \right] \\ 0 &= \frac{k_1 [A]_0}{k_2 - k_1} \frac{d}{dt} \left[ \left( e^{-k_1 t_{max}} - e^{-k_2 t_{max}} \right) \right] \\ &= \frac{k_1 [A]_0}{k_2 - k_1} \left( -k_1 e^{-k_1 t_{max}} + k_2 e^{-k_2 t_{max}} \right) \\ k_1 e^{-k_1 t_{max}} &= k_2 e^{-k_2 t_{max}} \\ e^{-(k_1 - k_2) t_{max}} &= \frac{k_2}{k_1} \\ -(k_1 - k_2) t_{max} &= \ln \left( \frac{k_2}{k_1} \right) \\ t_{max} &= \frac{1}{k_1 - k_2} \ln \left( \frac{k_1}{k_2} \right) \end{aligned} \quad (9.7.8)$$

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<sup>8</sup>This reaction is a special case since all stoichiometric coefficients are 1. If this were not the case, we would need to divide the species concentrations by their reaction coefficients to ensure an equality of this type holds.

Earlier in this section we noted that we could simplify the system of differential equations

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[I]}{dt} &= k_1[A] - k_2[I] \\ \frac{d[P]}{dt} &= k_2[I]\end{aligned}$$

by making two assumptions yet only ever mentioned one. The second assumption is that the concentration of I is *transient*, that is, it is slowly created and rapidly depleted so that [I] never “builds up” and we can approximate  $d[I]/dt \approx 0$ . This is also known as the *steady state approximation*. Then, by Equation (9.7.2).

$$\begin{aligned}0 &= k_1[A] - k_2[I] \\ [I] &= \frac{k_1[A]}{k_2} = \frac{k_1[A]_0}{k_2} e^{-k_1 t}\end{aligned}$$

which affords an expression for the concentration of P as a function of time by Equation (9.7.3):

$$[P] = k_2[I] = k_1[A]_0 e^{-k_1 t} \quad (9.7.9)$$

Thus, we see that using the steady state approximation affords an expression for the concentration of P as a function of time *consistent with the first-order decay of the reactant A*. An important aspect of the steady state approximation to keep in mind is that *it has nothing to do with equilibrium*. Although the concentration of intermediate is effectively constant, the concentrations of reactant and product are rapidly changing throughout the same interval of time.

## 9.8 Enzyme Kinetics

*Enzyme kinetics* is simply the study of enzymatic rates. In many cases, the rate of a reaction and how the rate changes in different conditions reveal the path followed by the reactants and are therefore indicative of the reaction mechanism. In all of our discussion on enzyme kinetics we’ll analyze reactions of the form



where E, S, ES, and P are the enzyme, substrate, enzyme-substrate complex, and product, respectively. The enzyme-substrate complex is sometimes also referred to as the Michaelis complex. Additionally, the rate constant  $k_2$  is sometimes also referred to as the *catalytic constant*, denoted  $k_{cat}$ .

### 9.8.1 The Michaelis-Menten Model

The kinetics of reaction (9.8.1) may be modeled simply and elegantly, using the *Michaelis-Menten model*, which estimates the formation of product from ES as a first-order process so that we have the rate,

$$\frac{d[P]}{dt} = k_2[ES] \quad (9.8.2)$$

also referred to as the *velocity* of reaction.<sup>9</sup> The *initial velocity*  $v_0$ , is then the rate of product formation at some initial time  $t = t_0$  where  $[ES] = [ES]_0$ . The overall rate of production of ES is the difference between rates

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<sup>9</sup>The “velocity” of a reaction, more generally, refers to the rate of product formation for any chemical reaction, not just enzyme catalysis.

of the elementary reactions leading to its appearance and those resulting in its disappearance:

$$\frac{d[\text{ES}]}{dt} = k_1[\text{E}][\text{S}] - (k_{-1} + k_2)[\text{ES}]$$

If we assume steady state for the concentration of ES just as we did in Section 9.7, this expression simplifies as,

$$\begin{aligned} k_1[\text{E}][\text{S}] &= (k_{-1} + k_2)[\text{ES}] \\ \frac{[\text{E}][\text{S}]}{[\text{ES}]} &= \frac{k_{-1} + k_2}{k_1} = K_m \end{aligned} \quad (9.8.3)$$

where  $K_m$  is referred to as the *Michaelis constant*. Note that although  $K_m$  looks a lot like a *dissociation constant*, it isn't quite the same because of the transformation of  $\text{ES} \xrightarrow{k_2} \text{E} + \text{P}$ . If the only reaction taking place was the reversible transformation  $\text{E} + \text{S} \rightleftharpoons \text{ES}$  then  $K_m$  would in fact be a dissociation constant, but this is not the case.

In general, the quantities  $[\text{ES}]$  and  $[\text{E}]$  are not easily measurable, however, the total enzyme concentration

$$[\text{E}]_{\text{T}} = [\text{ES}] + [\text{E}]$$

is usually known. The total enzyme concentration is equal to the initial enzyme concentration, also, unless more enzyme is added throughout the duration of a reaction. Though, I can't think of any reason why not all of the enzyme would be added at once. Thus, Equation (9.8.3) can be rewritten as

$$\begin{aligned} K_m[\text{ES}] &= [\text{E}][\text{S}] \\ K_m[\text{ES}] &= ([\text{E}]_{\text{T}} - [\text{ES}])[\text{S}] \\ [\text{ES}](K_m + [\text{S}]) &= [\text{E}]_{\text{T}}[\text{S}] \\ [\text{ES}] &= \frac{[\text{E}]_{\text{T}}[\text{S}]}{K_m + [\text{S}]} \end{aligned}$$

and substituting this result into Equation (9.8.2) affords the velocity of the reaction as a function of some directly measurable quantities:

$$v = \frac{d[\text{P}]}{dt} = \frac{k_2[\text{E}]_{\text{T}}[\text{S}]}{K_m + [\text{S}]} \quad (9.8.4)$$

The initial velocity of the reaction is a direct consequence of this expression, also:

$$v_0 = \frac{k_2[\text{E}]_0[\text{S}]_0}{K_m + [\text{S}]_0} \quad (9.8.5)$$

Equation (9.8.4) motivates us to define the point at which the *maximal velocity of reaction occurs*,  $v_{\text{max}}$ . The maximal velocity happens at high substrate concentrations when the enzyme is saturated, that is, when the enzyme is entirely in the ES form. Then,  $v_{\text{max}} = k_2[\text{E}]_0$  and we obtain,

$$v_0 = \frac{v_{\text{max}}[\text{S}]_0}{K_m + [\text{S}]_0} \quad (9.8.6)$$

known as the *Michaelis-Menten equation*. Equation (9.8.6) clearly illustrates the fact that the initial velocity of reaction is half-maximal when  $[\text{S}]_0 = K_m$

It's important to keep in mind that the Michaelis constant is unique for every substrate-enzyme pair. The magnitude of  $K_m$  varies widely with the identity of the enzyme and the nature of the substrate, as well as the

temperature and pH of the solution. We can express  $K_m$  in Equation (9.8.3) alternatively as

$$K_m = \frac{k_{-1}}{k_1} + \frac{k_2}{k_1} = K_s + \frac{k_2}{k_1} \quad (9.8.7)$$

where  $K_s$  is the dissociation constant of the enzyme-substrate complex. As  $K_s$  (and therefore also  $K_m$ ) *decreases*, the enzyme's affinity for a substrate *increases* so that we can think of  $K_m$  being a measure of the affinity of the enzyme for its substrate, provided that  $k_2/k_1$  is small compared to  $K_s$ .

In the beginning of this section I mentioned that  $k_2$  is sometimes also referred to as the catalytic constant,  $k_{cat}$ . More formally,  $k_{cat}$  is defined as,

$$k_{cat} = \frac{v_{max}}{[E]_0} \quad (9.8.8)$$

also known as the *turnover number*, because it is the number of reactions that each active site of the enzyme catalyzes per unit time. For enzymes with more complicated mechanisms than the one considered in the Michaelis-Menten model,  $k_{cat}$  is not always the same as  $k_2$ , and instead may be a function of several rate constants.

Keeping in mind that  $K_m$  is the concentration of substrate at which the velocity of the reaction is half-maximal, recognize that when  $[S] \ll K_m$ , very little ES is formed. Consequently,  $[E] \approx [E]_0$  so that Equation (9.8.5) reduces to

$$v_0 = \frac{k_2[E]_0[S]_0}{K_m} \approx \left( \frac{k_{cat}}{K_m} \right) [E][S]_0 \quad (9.8.9)$$

Here, the ratio  $k_{cat}/K_m$  acts as a second-order rate constant for the enzymatic reaction. In particular this ratio is a measure of the *catalytic efficiency* of the particular enzyme-substrate pair being studied. There is an upper limit on the catalytic efficiency known as the *diffusion-controlled limit*, near  $10^8$  to  $10^9 \text{ M}^{-1}\text{s}^{-1}$ . Enzyme-substrate pairs with  $k_{cat}/K_m$  ratios near this limit catalyze a reaction almost every time they encounter one another and hence have achieved a state of virtual catalytic perfection.

Here is an example problem regarding enzyme kinetics and some transition state theory. Imagine a hypothetical reaction,  $S \longrightarrow P$ , which has a rate constant  $k_1 = 10^{-6} \text{ s}^{-1}$  at  $T = 298.15 \text{ K}$ . Suppose the rate of reaction doubles when the reaction is performed at  $50^\circ\text{C}$  as opposed to  $25^\circ\text{C}$ . What is the enthalpy of activation? Using transition state theory we can compare these two reaction rates. Recall Equation (9.6.5) which allows us to write a ratio of the rate constants as

$$\begin{aligned} \frac{k_2}{k_1} &= \frac{\frac{k_B T_2}{h} \exp \{ -\Delta G^\ddagger / RT_2 \}}{\frac{k_B T_1}{h} \exp \{ -\Delta G^\ddagger / RT_1 \}} \\ &= \frac{T_2 \exp \{ -\Delta G^\ddagger / RT_2 \}}{T_1 \exp \{ -\Delta G^\ddagger / RT_1 \}} \end{aligned}$$

where  $k_2$  is the reaction rate when the temperature is raised, and  $T_1$  and  $T_2$  represent  $25^\circ\text{C}$  and  $50^\circ\text{C}$ , respectively. Importantly, notice that although the temperature is changing the change in Gibbs free energy to enter the transition state (which we can also think of as the activation energy) is *not* changing. Then, substituting

$k_2 = 2k_1$ , we can evaluate the enthalpy of activation:

$$\begin{aligned}\frac{2k_1}{k_1} &= \frac{T_2 \exp\{-\Delta G^\ddagger/RT_2\}}{T_1 \exp\{-\Delta G^\ddagger/RT_1\}} \\ \frac{2T_1}{T_2} &= \exp\left\{\frac{-(\Delta H^\ddagger - T_2\Delta S^\ddagger)}{RT_2} - \frac{-(\Delta H^\ddagger - T_1\Delta S^\ddagger)}{RT_1}\right\} \\ \frac{2T_1}{T_2} &= \exp\left\{\frac{-\Delta H^\ddagger}{RT_2} + \frac{\Delta H^\ddagger}{RT_1}\right\} \\ -R \ln\left(\frac{2T_1}{T_2}\right) &= \Delta H^\ddagger \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned}$$

Evaluating this expression at  $T_1 = 298.15$  K and  $T_2 = 323.15$  K as given in the problem affords  $\Delta H^\ddagger = 19.63$  kJ/mol as the enthalpy of activation for this reaction.

The one-way reaction illustrated above is nice, however, reality is rarely that simple. Suppose the substrate S can undergo an undesired reaction to a byproduct B, which occurs naturally at the rate  $k_b = 10^{-5} \text{ s}^{-1}$ . Fortunately, an enzyme E can accelerate the desired reaction  $E + S \longrightarrow ES \longrightarrow E + P$  with rate constant  $k_{cat} = 10^3 \text{ s}^{-1}$  and Michaelis constant  $K_M = 10 \text{ }\mu\text{M}$ . How much of this enzyme is needed to ensure that 99% of S is converted to P if  $[S]_0 = 1 \text{ mM}$  and  $T = 25^\circ\text{C}$ ? Here we'll need to consider the rates of reaction in either direction:

$$\begin{aligned}\frac{d[B]}{dt} &= k_b[S] \\ \frac{d[P]}{dt} &= k_{cat}[ES] = \frac{k_{cat}[E]_0[S]_0}{K_m + [S]_0}\end{aligned}$$

where Equation (9.8.6) was used to rewrite the rate of formation of the product P. Before continuing, notice that  $[S]_0 \gg K_M$  so that the denominator in the rate of formation of P is effectively just  $[S]_0$ . Then, finding the product ratio of the two products B and P is as simple as taking the ratio of their rates of formation:

$$\begin{aligned}\frac{d[B]/dt}{d[P]/dt} &= \frac{k_b[S]}{\frac{k_{cat}[E]_0[S]_0}{K_m + [S]_0}} \\ &\approx \frac{k_b[S]}{\frac{k_{cat}[E]_0[S]_0}{[S]_0}} \\ \frac{1}{99} &= \frac{k_b[S]}{k_{cat}[E]_0} \\ \frac{1}{99} &= \frac{(10^{-5} \text{ s}^{-1})(0.001 \text{ M})}{(10^3 \text{ s}^{-1})[E]_0} \\ [E]_0 &= 9.9 \times 10^{-10} \text{ M}\end{aligned}$$

Thus, we require that  $[E]_0 \approx 1 \text{ nM}$  in order to achieve 99% conversion to the desired product.

With the complication of a competing side reaction introduced, let's now ignore it. Instead, consider the free energy activation barrier of the reaction with and without an enzyme present. By how much does the enzyme lower the activation energy barrier for the  $S \longrightarrow P$  reaction at standard conditions? In other words, we're looking for the quantity  $\Delta\Delta G^\ddagger$ . Hopefully by now it's obvious, but to determine this quantity we'll turn

to transition state theory. In particular, the Eyring equation:

$$\begin{aligned}\frac{k_{cat}}{k_1} &= \exp \left\{ \frac{-\Delta\Delta G^\ddagger}{RT} \right\} \\ \Delta\Delta G^\ddagger &= -RT \ln \left( \frac{k_{cat}}{k_1} \right) \\ &= -(8.3145)(298.15) \ln \left( \frac{10^3}{10^{-6}} \right) \\ &= -51.37 \text{ kJ/mol}\end{aligned}$$

Thus, the enzyme lowers the free energy activation barrier by 51.37 kJ/mol. I'll also point out that the expression for the change in activation energy is nothing we haven't seen before due to detailed balance, with the relationship  $k_{cat}/k_1 = K_{eq}$ .

The tangent regarding detailed balance aside, suppose that we perform some more experiments and determine that the reaction rate with the enzyme present doubles from 25°C to 50°C. Given this information, calculate  $\Delta S_{cat}^\ddagger$ . The subtle yet important aspect to this question is recognizing that *the temperature dependence of the catalyzed reaction is the same as the uncatalyzed reaction*. That is to say, the enthalpy of activation is the same whether or not the enzyme is present. In the very first question we considered where we wanted to find the enthalpy of activation, we could ignore the entropy because its contribution does not change with temperature (again, refer to the Eyring equation). In this case, however, the change in entropy is (almost definitely) changing with the introduction of an enzyme because the substrate S must bind to it, therefore limiting its number of possible configurations. That is all to say, with the enzyme present we have  $\Delta H^\ddagger = 19.63$  kJ/mol and the change in entropy can be found by applying transition state theory to the catalyzed rate constant only at room temperature:

$$\begin{aligned}k_{cat} &= \frac{k_B T}{h} e^{-\Delta G_{cat}^\ddagger / RT} \\ \Delta G_{cat}^\ddagger &= -RT \ln \left( \frac{k_{cat} h}{k_B T} \right) \\ &= 55.9 \text{ kJ/mol}\end{aligned}$$

Now we can use the classical definition of the change in Gibbs free energy (along with the enthalpy of activation derived earlier) to find the change in entropy of the catalyzed transition state:

$$\begin{aligned}\Delta G_{cat}^\ddagger &= \Delta H_{cat}^\ddagger - T \Delta S_{cat}^\ddagger \\ 55.9 \text{ kJ/mol} &= 19.63 \text{ kJ/mol} - 298.15 \Delta S_{cat}^\ddagger \\ \Delta S_{cat}^\ddagger &= -121.65 \text{ J/mol}\end{aligned}$$

This is change in entropy for the catalyzed reaction to the transition state. I think it's amazing how all of these ideas and calculations we've done here rely on the theory that the reactants are in "equilibrium" with the transition state, even though in some aspects of organic chemistry we're taught to think that the transition state is necessarily a real state of the system, only an abstraction to help explain mechanisms.

Before finishing let's connect everything we've learned about this enzyme. In particular, describe in thermodynamic terms how this enzyme works to accelerate the reaction and propose a molecular mechanism as to how it might achieve this effect. Notice that we've already discussed two aspects of the system. Firstly, the enthalpy of activation is not changed upon introduction of the enzyme and secondly (which is almost a consequence of the first thing), the enzyme catalyzes the reaction by lowering the entropic barrier of the activated complex. So, we wouldn't be crazy to propose a mechanism that focuses on lowering the entropic barrier of the reaction. How could an enzyme do this? Intuitively, an enzyme limiting the number of configurations of a substrate makes sense (think "lock and key" model). In order to have a limited number of configurations



actually *help* the reaction proceed would require that the enzyme limits the substrate to configurations which closely resemble the activated state and final product (Hammond's postulate). So, we might propose that the mechanism used by the enzyme brings together functional groups of the substrate which are required to react in, thereby limiting the total possible number of microstates of the substrate while not losing any which encourage a reaction.

This is actually a commonly used strategy by enzymes, though it is seldom the case that lowering the entropic barrier is the *only* contribution to catalysis. An interesting case of an enzyme that does in fact ignore trying to change the enthalpic barrier, though, are ribosomes, which functions nearly exclusively by entropic catalysis.

### 9.8.2 Enzyme Inhibition

## 9.9 Single Molecule Kinetics

### 9.9.1 Förster Resonance Energy Transfer (FRET)

### 9.10 The Chapman Cycle

[http://www.columbia.edu/itc/chemistry/chem-c2407/hw/ozone\\_kinetics.pdf](http://www.columbia.edu/itc/chemistry/chem-c2407/hw/ozone_kinetics.pdf)

[http://irina.eas.gatech.edu/ATOC3500\\_Fall1998/Lecture35.pdf](http://irina.eas.gatech.edu/ATOC3500_Fall1998/Lecture35.pdf)

## Part II

# Quantum Mechanics

## CHAPTER

# 10

# TRANSITIONING FROM CLASSICAL TO QUANTUM PHYSICS

*My favorite deep, elegant and beautiful explanation is Albert Einstein's 1905 proposal that light consists of energy quanta, today called photons. Actually, it is little known, even among physicists, but extremely interesting how Einstein came to this position. It is often said that Einstein invented the concept to explain the photoelectric effect. Certainly, that is part of Einstein's 1905 publication, but only towards its end. The idea itself is much deeper, more elegant and, yes, more beautiful.*

- Anton Zeilinger

By the end of the nineteenth century, many scientists believed that all of the fundamental discoveries of science had been made and little remained except for improving experimental methods and measuring physical constants to a greater number of decimal places. This attitude was justified by the accomplishments within both chemistry and physics, such as Mendeleev's development of the periodic table and Gibbs' complete development of the field of thermodynamics.

It wasn't until scientists began to investigate the properties of matter at the atomic level that they realized classical mechanical models failed to predict the behavior of atoms and the outcomes of some experiments. Ernest Rutherford's nuclear model of the atom posited an atomic structure consisting of a small, dense, positively charged core with negatively charged electrons orbiting the nucleus. This model agreed with his experimental results, unlike the previously established "plum-pudding model" which proposed that electrons were embedded in a sphere of positive charge. Using classical mechanics to try and explain this structure was fruitless. Which forces held the nucleus together? What stopped the orbiting electrons from spiraling into the nucleus? These questions explored a small fraction of the discrepancies between the nuclear model of the atom and classical mechanics yet were enough to prompt a generation of scientists to remedy this disaccord.

## 10.1 The Photoelectric Effect

The emission of electrons from a substance due to light striking its surface is referred to as the *photoelectric effect*. The discovery of the photoelectric effect did not pose a difficulty for classical mechanics. Thermal

emission, the process by which a metal heated to a sufficiently high temperature emits electrons, had been known of for a while and paralleled this effect nicely. What classical mechanics could not predict, however, was the dependency the emission of electrons had on the frequency of light shined on the material.

In the year 1900, Max Planck determined that he could calculate the emission spectrum of electrons by this effect perfectly by assuming that oscillating atoms were *not* free to have any energy and instead have specific energies, corresponding to integer multiples of one another. More technically, Planck postulated that the energy emitted by these excited electrons was *quantized*, unlike the model from classical mechanics which predicts that the emission spectrum would be continuous.

Planck was the first to hypothesize that each quantized packet of light (or just a *quantum* of light) had an energy directly proportional to the frequency, given by

$$E = h\nu \quad (10.1.1)$$

where  $h = 6.62607 \times 10^{-34}$  J s is Planck's constant,  $\nu$  is the frequency of the incident light, and  $E$  is the energy of the wave packet. A spatially localized quantum of light is often referred to as a *photon*. Using this idea, Albert Einstein postulated more generally about light quanta and their interaction with matter:

1. Light of frequency  $\nu$  constitutes discrete quanta, each of energy  $E = h\nu$ . Each photon is traveling at the speed of light  $c$ .
2. Light quanta are emitted or absorbed on an all-or-nothing basis. A substance can emit any integer number of quanta but never any fractional or irrational number. Similarly, an electron in a material can never absorb a non-integer number of quanta.
3. A light quantum, when absorbed by a metal, delivers its entire energy to *one* electron.

Invoking energy conservation, these postulates allow us to calculate the total kinetic energy of an emitted electron from the following relationship:

$$h\nu = \phi_0 + E \quad (10.1.2)$$

Here,  $h\nu$  is the energy of the photon incident to the electron,  $\phi_0$  is the *work function*, or the ionization energy of the electron, and  $E$  represents the total energy left in the emitted electron (for all intents and purposes this can be thought of as the total kinetic energy). A plot of this equation is illustrated in Figure 10.1.

The ideas put forth by Einstein within these postulates—that light comes in chunks, the chunks cannot be divided, and the energy of one chunk is delivered to one electron—were directly at odds with the ideas of classical physics where energy can be continuously divided and shared. Hence, they are crucial to an understanding of quantum mechanics.

The idea of a quantized packet of light leads us to believe that light behaves as a *particle*, traveling in straight lines as rays of light. As we'll see, depending on the experiment we perform we may attain results which agree with this assumption and we may attain results which go against it.

## 10.2 Specific Heat Models

Soon after working on the photoelectric effect, Einstein (among others) used the concept of energy quantization to model molar heat capacities more successfully than had been done using classical physics.

The standard classical result for the heat capacity of one mole of atoms vibrating about their equilibrium lattice positions of a solid is the *Law of Dulong-Petite*<sup>1</sup>, which asserts that  $C_V = 3R$ , where  $R$  is the molar gas constant. Importantly, this result occurs at higher temperatures and is typically a better representation for

<sup>1</sup>During the first half of the nineteenth century this law was used to get rough values of the atomic weights of some elements.

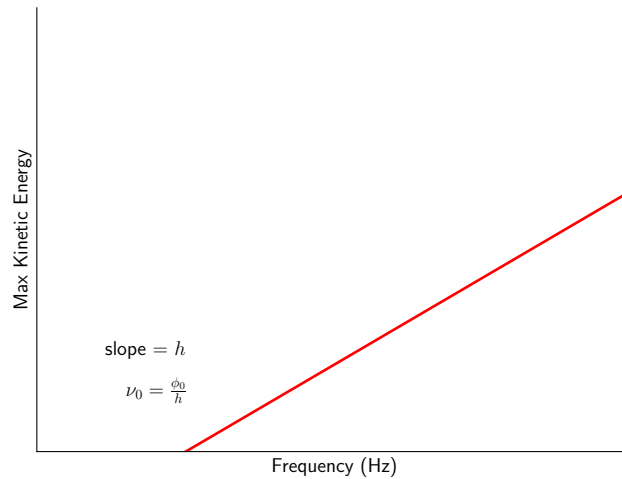


Figure 10.1: The maximum kinetic energy attainable by an electron with a work function  $\phi_0$  after being excited by a photon of light with energy  $h\nu$ . The frequency  $\nu_0$  represents the minimum frequency of light required for an electron to be emitted. The slope of the line is Planck's constant  $h$ .

heavier elements, such as iron, nickel, or silver. Since this law doesn't do very well for lighter elements, there are procedures such as *Kopp's Rule* which afford the specific heats for those lighter elements at high enough temperatures.

As mentioned, the Law of Dulong-Petite occurs at high temperatures yet from experiment we know that  $C_V$  decreases to zero as the temperature is lowered. Upon assuming that the oscillations of atoms about their equilibrium positions were quantized according to Planck's relation  $E = h\nu$ , Einstein was able to achieve excellent agreement with experimental data for the heat capacity of solids, far better than what was predicted by classical physics. In particular, he made the simplifying assumption that all atoms vibrated inside the solid independently of one another and at the same frequency. The plot of his equation is shown in Figure 10.2.

It's important to notice Einstein assumed *mechanical vibrations* of the atoms were subject to quantization so that under this model, solids were viewed as a lattice of quantum harmonic oscillators all of the same frequency. This type of quantization is an excellent description of *optical phonons*<sup>2</sup>.

Although Einstein achieved far better agreement with experimental heat capacity data than could classical physics, his model faltered as the temperature of the solid decreased to zero. This was due in part to the fact that his assumptions resulted in the oscillations of all atoms in a solid being independent of one another, whereas the correct behavior is found by quantizing the *normal modes* of the solid, i.e., the mode of a system in which all parts of a system move sinusoidally with the same frequency and phase. This kind of quantization is accounted for in the Debye model.

No matter the model for the heat capacity or representation of atoms within a lattice, both Debye and Einstein extended the applicability of quantum mechanics from radiation, where it was conceived, to molecular kinetic theory, to which radiation was not directly related. The significance of these achievements is so great, in fact, that in 1911 Walther Nernst (the man for which the *Nernst Equation* inherits its name) declared

At present, quantum theory is essentially only a rule for calculation, of apparently a very strange, one might even say grotesque, nature; but it has proven so fruitful by the work of Planck, as far as radiation is concerned, and by the work of Einstein, as far as molecular mechanics is concerned... that it is the duty of science to take it seriously and to subject it to careful investigations.

<sup>2</sup>*Phonons* are a unit of vibrational energy that arise from oscillating atoms within a crystal. Just as *photons* are electromagnetic waves, *phonons* can be thought of as mechanical waves. They are analogous to photons in that they describe packets of energy that come from waves traveling through a solid. In this way, we can think of phonons as particles of sound just as photons are particles of light.

If this wasn't enough, Karl Taylor Compton (former physicist and president of MIT) remarked that Einstein's development of quantum theory was "a contribution to physical theory certainly comparable in importance, and thus far more useful in its applications than his more impressive and wider publicized general theory of relativity."

### 10.2.1 Einstein Model for Specific Heat

As mentioned, the Einstein model for specific heat models a crystal lattice as atoms vibrating at the same frequency, subject to energy quantization. Then, all of these quantum harmonic oscillators have an energy of the form  $E = n(h\nu)$  for some integer  $n$ . The average energy of an oscillator is then determined as

$$\langle E \rangle = \frac{3Nh\nu}{e^{h\nu/k_B T} - 1}$$

where  $N$  is Avogadro's constant and a factor of 3 is added to account for all possible directions of translational motion. Recall that the heat capacity at a constant volume is equivalent to the partial derivative of the internal energy with respect to time,  $C_V = \partial E / \partial T$  so that we have

$$\begin{aligned} C_V &= \frac{\partial \langle E \rangle}{\partial T} \\ &= \frac{\partial}{\partial T} \left[ \frac{3Nh\nu}{e^{h\nu/k_B T} - 1} \right] \\ &= \frac{3Nh\nu(h\nu/k_B T^2)e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2} \\ &= \frac{3R(h\nu/k_B T)^2 e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2} \end{aligned} \quad (10.2.1)$$

where in the last line we've taken advantage of the fact that  $k_B N = R$  for the ideal gas constant  $R$ . Equation (??) is the Einstein equation for the heat capacity. Notice that in the limit that the temperature becomes infinitely large, this expression converges to  $3R$ , in accordance with the Law of Dulong-Petite.

If a crystal could be described by atoms vibrating uniformly at a single frequency, this model would work great! This, however, is not the case. The assumption breaks down at extremely low temperatures where the vibrations of atoms within a crystal are distributed across some spectrum of frequencies. Modifications to the theory to relax such assumptions and include ultracold behavior can be found by the Debye model.

### 10.2.2 Debye Model for Specific Heat

Developed by Peter Debye, the Debye model for the specific heat of elemental solids treats the vibrations of atoms as phonons in a box, unlike the Einstein model which treats atoms as non-interacting quantum harmonic oscillators. In other words, instead of treating the atoms as independent harmonic oscillators, Debye treated the phonon moving through the solid as a harmonic oscillator.

The equation for the heat capacity at a constant volume found by Debye can be expressed as

$$C_V = 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (10.2.2)$$

where  $\theta_D$  is referred to as the *characteristic temperature* with corresponding units. At high enough temperatures,

the ratio  $\theta_D/T \approx 0$  so that (after some fancy integral approximations) the model simplifies as

$$\begin{aligned} C_V &= 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \\ &\approx 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^2 dx \\ &= 9R \left( \frac{T}{\theta_D} \right)^3 \frac{1}{3} \left( \frac{\theta_D}{T} \right)^3 \\ &= 3R \end{aligned}$$

affording the classical result. At low temperatures, the ratio  $\theta_D/T \rightarrow \infty$  so that our integral simplifies as

$$C_V = 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = 9R \left( \frac{T}{\theta_D} \right)^3 \left( \frac{4\pi^4}{15} \right) = \frac{12\pi^4 R}{5\theta_D^3} T^3$$

so that near  $T \approx 0$ , the Debye formula for the heat capacity goes as  $C_V \sim T^3$ . This result correctly predicts the temperature dependence of  $C_V$ , affording the name the *Debye  $T^3$  Law*.

A plot of the Debye model and Einstein models are shown in Figure 10.2. In both the limits as the temperature goes to zero and shoots off to infinity the graphs agrees with the classical result. While predicting heat capacities at low temperatures is great and all, the simplifying assumptions made by Debye cause the model to falter at intermediate temperatures, unlike the Einstein model.

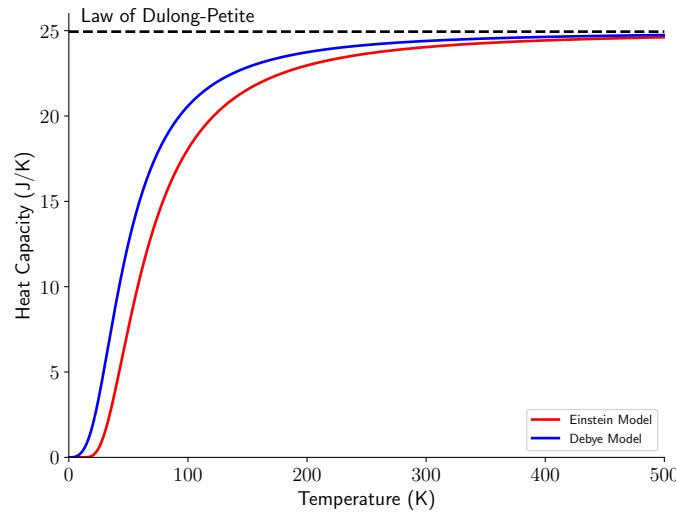


Figure 10.2: The specific heat of atomic solids as predicted by Debye and Einstein. Both models agree with the classical result for the heat capacity as temperature increases to infinity. The Debye model accurately predicts  $C_V$  at low temperatures while the Einstein model does better at intermediate temperatures.

## 10.3 Blackbody Radiation

A *blackbody* serves as an idealized radiating material which can absorb and emit all frequencies of light. We're all familiar with radiating bodies, such as a stove top that turns red after being heated before turning white and then blue as more heat is added to the material. In terms of frequencies, the radiation emitted by the stove goes from a lower frequency (red light) to a higher frequency (blue light) as the temperature increases.

Using classical mechanics we can derive an expression for the frequencies of light radiated from a blackbody

and their relative magnitudes:

$$\rho(\nu, T)d\nu = \frac{8\pi k_B T}{c^3} \nu^2 d\nu \quad (10.3.1)$$

In Equation (10.3.1),  $\rho$  is the *spectral density* and is a function of wavelength  $\nu$  and temperature  $T$ , measured in Kelvin, and  $c$  is the speed of light. This law is also referred to as the *Rayleigh-Jeans law*. The factor  $d\nu$  is used on both sides of the equation because we are interested in the energy density between  $\nu$  and  $\nu + d\nu$ . By inspection, we can see that we'd expect the spectral density to diverge as  $\nu \rightarrow \infty$ . In other words, classical theory predicts that as  $\nu \rightarrow \infty$  the blackbody should emit an infinite amount of energy. Then, in theory, all blackbodies should emit an infinite amount of energy at temperatures above absolute zero. The failure of classical mechanics to accurately model the behavior blackbodies was deemed the *ultraviolet catastrophe*.

Another way of writing Equation (10.3.1) is

$$\rho(\nu, T)d\nu = \left( 2 \times \frac{4\pi\nu^2}{c^3} \times k_B T \right) d\nu$$

where, the term  $k_B T$  represents the average kinetic energy contributed by the wave oscillations<sup>3</sup>, the factor of 2 out front accounts for the transverse nature of the wave and the fact that it has two possible polarizations, and the term  $4\pi\nu^2/c^3$  is the number of waves of frequency  $\nu$  per unit frequency per unit volume that satisfy the boundary conditions.

Planck was the first scientist to offer an explanation for blackbody radiation which was consistent with experimental results. Using his idea of energy quantization alongside some statistical thermodynamic ideas<sup>4</sup>, he derived the equation,

$$\rho(\nu, T)d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} \quad (10.3.2)$$

known as the *Planck distribution law for blackbody radiation*. For small enough frequencies, Equations (10.3.1) and (10.3.2) become identical, however, for larger frequencies Planck's distribution does not diverge. Moreover, Planck's distribution agrees with the *Stefan-Boltzmann power law*, as well as the *Wien displacement law*, two relationships which had been confirmed empirically long before the ultraviolet catastrophe was remedied. A plot of this distribution can be seen in Figure 10.3a for different temperatures.

Planck's distribution can also be written in terms of wavelengths, using the relationship  $\nu = c/\lambda$ . From this, we find that  $d\nu/d\lambda = -c/\lambda^2$  so that Equation (10.3.2) can be rewritten as

$$\rho(\lambda, T)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/(\lambda k_B T)} - 1} \quad (10.3.3)$$

For large and small enough wavelengths the same equalities hold as the corresponding equation as a function of frequency since Equations (10.3.2) and (10.3.3) are mathematically equivalent. A plot of the spectral density as a function of wavelength is illustrated in Figure 10.3b for some different temperatures.

The theory of blackbody radiation and the Planck distribution for blackbody radiation is used commonly in astronomy to estimate the surface temperature of stars. In fact, Equation (10.3.2) has been used to model the surface temperature of our sun as well as stars which are much farther away and much hotter.

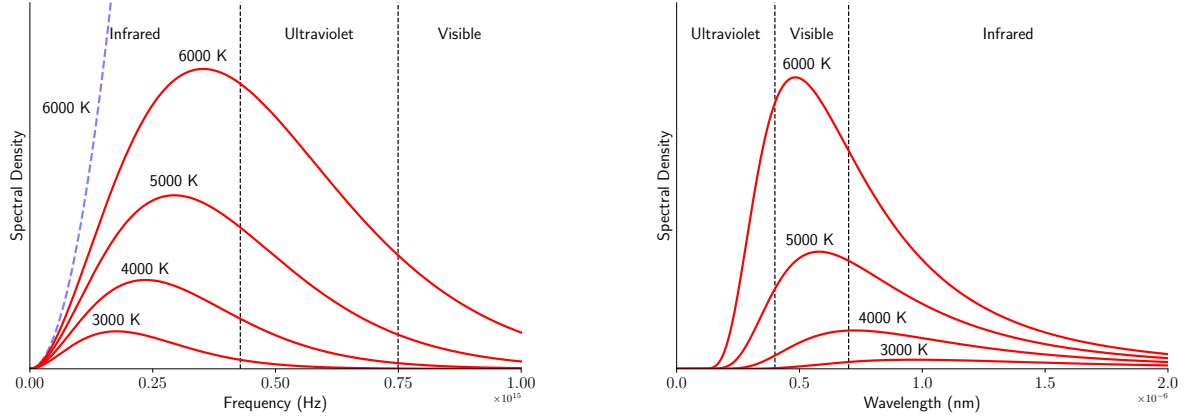
### Planck's Derivation

An important preface to this section is the fact that at the time of derivation, Planck was most likely unaware of the Rayleigh-Jeans law, that is, the distribution of the spectral density of a blackbody based on classical

<sup>3</sup>This is a result of equipartition from statistical mechanics.

<sup>4</sup>namely, the theorem of equipartition based on statistical mechanics





(a) Plot of spectral density as a function of frequency. As frequency increases, the energy emitted by the blackbody increases. (b) Plot of spectral density as a function of wavelength. As wavelength increases, the energy emitted by the blackbody decreases.

Figure 10.3: Plots of the Planck distribution for blackbody radiation as a function of frequency and wavelength at different temperatures. As we can see from both plots, increasing the temperature increases the amount of energy emitted by the blackbody.

physics. Instead of working from this expression, then, he based his effort on *Wien's law*, given as

$$\rho(\nu, T) = \alpha \nu^3 e^{-\beta \nu / T} \quad (10.3.4)$$

for some constants  $\alpha$  and  $\beta$ .<sup>5</sup> Equation (10.3.4) was supported experimentally for light within the visible spectrum and temperatures up to 4000 K, though, at lower frequencies it failed to correctly predict the behavior of blackbody radiation.

Planck started with three important experimental results: (1) Wien's law was correct for large enough frequencies, (2) Wien's *displacement* law was in general correct, and (3) at small enough frequencies, the radiation density of a blackbody is proportional to  $T$ . Using these results and the ideas of statistical mechanics from Boltzmann, his initial attempts to derive a blackbody radiation were based on the entropy that could be defined for such radiation. In particular, he was tasked with deriving an entropy for the waves of frequency  $\nu$ , then multiplying by the *number* of waves of frequency  $\nu$  per unit frequency per unit volume. This latter factor is the *number of normal modes of the radiation*.

Recall from statistical mechanics the Boltzmann equation. For  $N$  identical systems (in our case  $N$  is the number of copies of a particular radiation wave) we have that the entropy is given by

$$S = \frac{k_B}{N} \ln W \quad (10.3.5)$$

for the number of microstates  $W$  of the system. Among these  $N$  waves, there must be a total amount of energy  $E = N \langle E \rangle$  for the average energy of a single system  $\langle E \rangle$  by definition of the average. Keeping in the theme of Boltzmann, Planck next assumed that energy could be discretized for the purposes of counting with an intention of taking a limit at the end of the calculation. For a discrete quantum of energy  $\varepsilon$ , the number of ways to distribute  $P = E/\varepsilon$  elements of energy among  $N$  waves becomes<sup>6</sup>

$$W = \binom{P + N - 1}{P} = \frac{(P + N - 1)!}{P!(N - 1)!}$$

Determining the logarithm of this expression for Equation (10.3.5) can be done by Stirling's Approximation,

<sup>5</sup>Note that *Wein's law* and *Wein's displacement law* are two different equations.

<sup>6</sup>Counting the number of ways to do this is analogous to the *balls in boxes* or *stars and bars* problem commonly encountered in combinatorics.

$\ln n! = n \ln n - n$ . So, ignoring the factor of 1 because it is negligible compared to the magnitudes of  $P$  and  $N$ , we have that

$$\begin{aligned}
S &= \frac{k_B}{N} \ln W \\
&= \frac{k_B}{N} \left[ \ln \left( \frac{(P+N)!}{P!N!} \right) \right] \\
&= \frac{k_B}{N} [\ln(P+N)! - \ln P! - \ln N!] \\
&\approx \frac{k_B}{N} [(P+N) \ln(P+N) - (P+N) - P \ln P + P - N \ln N + N] \\
&= \frac{k_B}{N} [(P+N) \ln(P+N) - P \ln P - N \ln N] \\
&= k_B \left[ \left( \frac{P}{N} + 1 \right) \ln(P+N) - \frac{P}{N} \ln P - \ln N \right] \\
&= k_B \left[ \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \ln \left[ N \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \right] - \frac{\langle E \rangle}{\varepsilon} \ln \left( N \frac{\langle E \rangle}{\varepsilon} \right) - \ln N \right] \\
&= k_B \left[ \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) + \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \ln N - \frac{\langle E \rangle}{\varepsilon} \ln \left( N \frac{\langle E \rangle}{\varepsilon} \right) - \ln N \right] \\
&= k_B \left[ \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) + \frac{\langle E \rangle}{\varepsilon} \ln N + \ln N - \frac{\langle E \rangle}{\varepsilon} \ln \left( \frac{\langle E \rangle}{\varepsilon} \right) - \frac{\langle E \rangle}{\varepsilon} \ln N - \ln N \right] \\
&= k_B \left[ \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) - \frac{\langle E \rangle}{\varepsilon} \ln \frac{\langle E \rangle}{\varepsilon} \right]
\end{aligned}$$

The seventh line above takes advantage of the relationship  $PN = \langle E \rangle / \varepsilon$ . At this point, we can take the derivative of this expression with respect to the average energy to find that

$$\begin{aligned}
\frac{dS}{d\langle E \rangle} &= k_B \frac{d}{d\langle E \rangle} \left[ \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) - \frac{\langle E \rangle}{\varepsilon} \ln \frac{\langle E \rangle}{\varepsilon} \right] \\
&= k_B \left[ \frac{1}{\varepsilon} \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) + \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) \frac{\frac{1}{\varepsilon}}{\frac{\langle E \rangle}{\varepsilon} + 1} - \left( \frac{1}{\varepsilon} \ln \frac{\langle E \rangle}{\varepsilon} + \frac{\langle E \rangle}{\varepsilon} \frac{\frac{1}{\varepsilon}}{\frac{\langle E \rangle}{\varepsilon}} \right) \right] \\
&= k_B \left[ \frac{1}{\varepsilon} \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) + \frac{1}{\varepsilon} - \left( \frac{1}{\varepsilon} \ln \frac{\langle E \rangle}{\varepsilon} + \frac{1}{\varepsilon} \right) \right] \\
&= \frac{k_B}{\varepsilon} \left[ \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) - \ln \frac{\langle E \rangle}{\varepsilon} \right] \tag{10.3.6}
\end{aligned}$$

Taking a brief detour, we can relate the derivative of the entropy with respect to energy in an alternate fashion using thermodynamics. Using the first law, and assuming that radiation is not performing any work, we have that

$$dE = dq + dw = TdS + PdV \Rightarrow \frac{dS}{dE} = \frac{1}{T} \tag{10.3.7}$$

which allows us to relate Equation (10.3.6) to the reciprocal of the temperature as

$$\frac{k_B}{\varepsilon} \left[ \ln \left( \frac{\langle E \rangle}{\varepsilon} + 1 \right) - \ln \frac{\langle E \rangle}{\varepsilon} \right] = \frac{1}{T}$$

affording an expression for the average energy, after some algebraic gymnastics, as

$$\langle E \rangle = \frac{\varepsilon}{e^{\varepsilon/k_B T} - 1} \tag{10.3.8}$$

Note that this is the *average* energy, and to determine the *total* energy we first must find the number of copies  $N$  of a particular wave, defined previously. This equates to counting the number of possible normal modes of a wave at a given frequency within a given region of space. This involves some quantum antics we have

not quite learned, so I'll just tell you that  $N = 8\pi\nu^2/c^3$ , just as its written in Equation (10.3.2). Multiplying Equation (10.3.8) by this value for  $N$  affords Equation (10.3.2) as desired.

### 10.3.1 The Stefan-Boltzmann Power Law

The Stefan-Boltzmann power law describes the power radiated from a blackbody in terms of its temperature and can be expressed as

$$W = \sigma T^4 \quad (10.3.9)$$

where  $W$  is the total energy radiated per unit surface area,  $T$  is the temperature of the material, and  $\sigma$  is the Stefan-Boltzmann constant, defined as

$$\sigma = \frac{2\pi^5 k_B^4}{15c^2 h^3} \approx 5.67074 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4} \quad (10.3.10)$$

It can be shown from thermodynamic arguments that the total energy radiated per volume, i.e., the energy density, is related to  $W$  by

$$E_V = \frac{4}{c} W \quad (10.3.11)$$

where  $E_V = E_{\text{total}}/V$  for a total energy and volume of a blackbody  $E_{\text{total}}$  and  $V$ .

To derive the Stefan-Boltzmann power law from Planck's distribution we first need to convert Equation (10.3.2) from representing a spectral density to representing a spectral intensity. Luckily, this can be done with ease after scaling the density by some constants.

$$I(\nu, T) = \frac{c}{4\pi} \rho(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/k_B T} - 1} \quad (10.3.12)$$

The conversion is weird but can be understood with a small amount of background. The intensity  $I(\nu, T)$  is defined as the power emitted per area, per steradian, per frequency. Additionally, the spectral density  $\rho(\nu, T)$  is defined as the energy per volume per frequency. Symbolically,

$$\frac{\text{energy}}{\text{area} \cdot \text{time} \cdot \text{steradian} \cdot \text{frequency}} = \frac{\text{energy}}{\text{volume} \cdot \text{frequency}} \quad (10.3.13)$$

Getting rid of steradians in the denominator can be done by scaling the spectral density by a factor of  $1/4\pi$ , the number of steradians in the unit sphere. Also, going from  $1/(\text{area} \cdot \text{time})$  to  $1/\text{volume}$  can be done by scaling by a factor with units distance/time, i.e., the speed of light  $c$ . This is where the factor of  $c/4\pi$  comes from in Equation (10.3.12). Also, a more detailed discussion of steradians and solid angles can be found in Appendix ??.

Now, to attain the total energy radiated per unit surface area we'll consider the integral

$$W = \iiint I(\nu, T) \cos \varphi d\nu d\Omega \quad (10.3.14)$$

where  $I(\nu, T)$  is defined as above and  $d\Omega = \sin \varphi d\varphi d\theta$  is the *solid angle* corresponding to a differential area on the surface of the sphere. The solid angle can be thought of as the area of the sphere covered by a cone emanating from the center of the sphere. The factor of  $\cos \varphi$  is included because the intensity is proportional to the cosine of the angle between the incident photon and the normal vector to the surface of the sphere<sup>7</sup>.

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<sup>7</sup>This is known as *Lambert's cosine law*. A surface which obeys this principle is referred to as *Lambertian*.

With that, we can integrate the expression above over all frequencies and

$$\begin{aligned}
 W &= \int_0^\infty I(\nu, T) d\nu \int_0^{2\pi} \int_0^{\pi/2} \cos \varphi \sin \varphi d\varphi d\theta \\
 &= \left( \int_0^\infty \frac{2h}{c^2} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} \right) \left( 2\pi \int_0^{\pi/2} \cos \varphi \sin \varphi d\varphi \right) \\
 &= \left( \frac{2h}{c^2} \int_0^\infty \frac{\nu^3}{e^{h\nu/k_B T} - 1} d\nu \right) \left( 2\pi \left[ \frac{1}{2} \sin^2 \varphi \right]_0^{\pi/2} \right) \\
 &= \frac{2\pi h}{c^2} \int_0^\infty \frac{\nu^3}{e^{h\nu/k_B T} - 1} d\nu
 \end{aligned}$$

To evaluate this integral we'll make the substitution  $u = h\nu/k_B T$  and therefore  $d\nu = (k_B T/h) du$ . Then,

$$\begin{aligned}
 W &= \frac{2\pi h}{c^2} \int_0^\infty \frac{\left(\frac{k_B T u}{h}\right)^3}{e^u - 1} \left(\frac{k_B T}{h}\right) du \\
 &= \frac{2\pi h}{c^2} \left(\frac{k_B T}{h}\right)^4 \int_0^\infty \frac{u^3}{e^u - 1} du
 \end{aligned}$$

This resultant integral goes by a few different names, all of which are not simple to solve and make me question my decision to study chemistry. In any case, it evaluates to

$$W = \frac{2\pi h}{c^2} \left(\frac{k_B T}{h}\right)^4 \left(\frac{\pi^4}{15}\right) = \frac{2\pi^5 k_B^4 T^4}{15c^2 h^3} = \sigma T^4$$

which agrees with the Stefan-Boltzmann law introduced in the beginning.

### 10.3.2 The Wien Displacement Law

The Wien displacement law asserts that the blackbody radiation curve at some temperature will peak at different wavelengths which are proportional to the temperature.

$$\lambda_{\max} = \frac{b}{T} \quad (10.3.15)$$

$b$  is *Wien's displacement constant* and is approximately  $b \approx 2.89777 \times 10^{-3}$  m K. The inverse dependence of the wavelength with temperature is something that everyone has observed. As objects heat up they begin by turning red and orange before turning to blue. This is equivalent to the wavelength decreasing as the temperature increases.

Deriving Wien's law is simpler than one might imagine. We can use Planck's distribution for blackbody radiation as a function of the wavelength and differentiate with respect to the wavelength to determine where the spectral density peaks. Beginning by differentiating Equation (10.3.3) and setting the derivative equal to zero,

$$\begin{aligned}
 \frac{d\rho(\lambda, T)}{d\lambda} &= \frac{d}{d\lambda} \left[ \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/(\lambda k_B T)} - 1} \right] \\
 0 &= 8\pi hc \left( \frac{-5}{\lambda^6 (e^{hc/(\lambda k_B T)} - 1)} - \frac{\frac{-hc}{\lambda^2 k_B T} e^{hc/(\lambda k_B T)}}{\lambda^5 (e^{hc/(\lambda k_B T)} - 1)^2} \right) \\
 &= \frac{hc}{\lambda^7 k_B T} \frac{e^{hc/(\lambda k_B T)}}{(e^{hc/(\lambda k_B T)} - 1)^2} - \frac{1}{\lambda^6} \frac{5}{(e^{hc/(\lambda k_B T)} - 1)} \\
 &= \frac{hc}{\lambda k_B T} \frac{e^{hc/(\lambda k_B T)}}{e^{hc/(\lambda k_B T)} - 1} - 5
 \end{aligned}$$

Here we're allowed the substitution  $u = hc/(\lambda k_B T)$  to make solving this equation less cumbersome:

$$\begin{aligned} 0 &= \frac{ue^u}{u-1} - 5 \\ ue^u &= 5(u-1) \\ 0 &= (u-5)e^u + 5 \end{aligned}$$

The best way I can think to solve this equation is simply to graph it. The plot is illustrated in Figure 10.4. As shown in the plot, the solution to this equation is  $u = 0$  (the trivial solution) and  $u = 4.96511$ . Hence, we have that

$$u = 4.96511 = \frac{hc}{\lambda_{\max} k_B T} \Rightarrow \lambda_{\max} = \frac{hc}{4.96511 T} = \frac{b}{T}$$

with  $b = 2.89777 \times 10^{-3}$  which agrees with the known value.

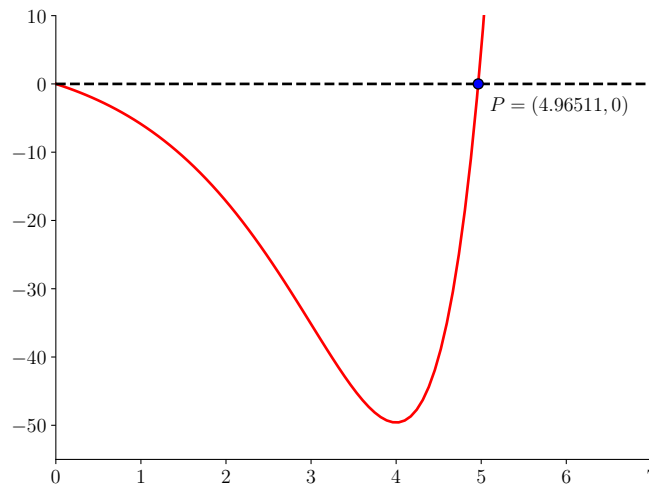


Figure 10.4: Plot of  $y = (x - 5)e^x + 5$ .

## 10.4 The Double Slit Experiment

It's been said that there is no single experiment that exhibits the surprising nature of quantum mechanics as well as the diffraction of particles by a double slit. The experimental setup is relatively simple. A phosphorescent screen which flashes when struck by light is parallel to a metal screen with two small slits cut out of it to allow light to pass through. The size of the slits is far less than the distance between the phosphorescent and metal screens and over the course of the experiment we are always shining just one photon on the screen at a time.

If we simplified our lives for a moment and considered the case of a metal screen with only one slit, the distribution of light on the phosphorescent screen illustrates maxima and minima similar to the maxima and minima created by wave interference, as illustrated in the upper half of Figure 10.5.

Now, we introduce two slits to the metal screen so that the light detected from the phosphorescent screen will be a combination of the two slits. The results of this experiment are shown in the lower half of Figure 10.5. Immediately, there are some obvious differences and similarities between the experiments. In the case of both the double and single slit, the spatial distribution of the light flashes indicate that the photons are behaving as waves yet individual flashes are observed on the phosphorescent screen as expected from a particle. Recall that initially we said we only allow a single packet of light to pass through the slits at a time. So, it seems as

though the photons are behaving as both waves and particles simultaneously in the case of the double slit!

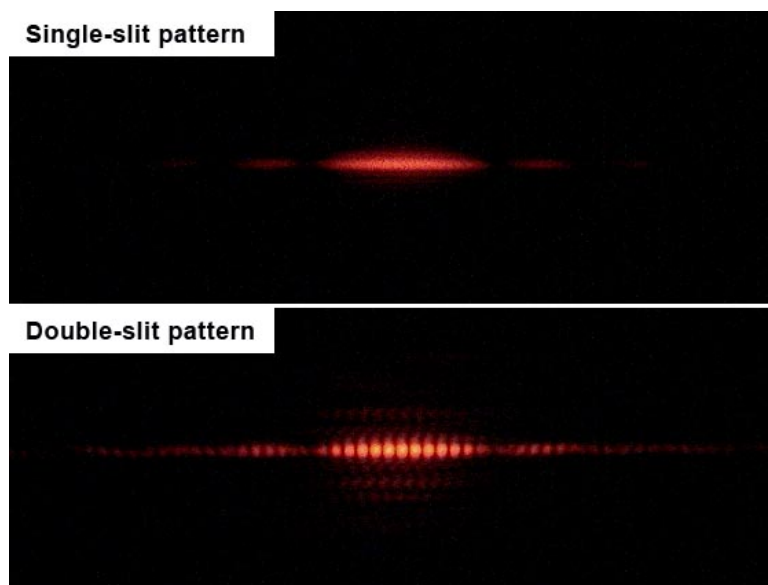


Figure 10.5: Results of the diffraction experiment with one and two slits.

Through the lens of classical mechanics we could arrive at one of two results. Either, individual electrons are moving through the slits to generate the points on the light screen to generate the distribution of light, or, the spatial distribution of light is governed by a diffraction pattern. The former behavior is particle-like and the latter wave-like. Whereas in classical mechanics we would need to choose one *or* the other, in quantum mechanics we can choose to say the behavior of electrons is particle-like *and* wave-like. Using a more technical quantum mechanical description we'd say that the distribution of electrons incident to the phosphorescent screen is a superposition of waves going through the top and bottom slits, which is equivalent to saying the electron is going through both slits simultaneously.

This experiment, alongside the others discussed in this chapter, constitutes an introduction to *wave-particle duality*, the idea that every elementary particle may be described as either a particle or a wave. Regarding the topic, Albert Einstein wrote

It seems as though we must use sometimes the one theory and sometimes the other, while at times we may use either. We are faced with a new kind of difficulty. We have two contradictory pictures of reality; separately neither of them fully explains the phenomena of light, but together they do.

That's all to say, quantum mechanics is weird and anyone who says they understand it is lying.

## 10.5 Matter Waves

Building off of Einstein's theories regarding wave-particle duality, Prince Louis-Victor de Broglie thought that if light waves could exhibit particle-like behavior then why can't all material particles exhibit wave-like behavior? That is, what about the existence of *matter waves*? With no experimental evidence to support his claim, de Broglie postulated that *if* (emphasis on the if) a material particle of momentum  $p = mv$  has wave-like nature, then its wavelength must be given by

$$\lambda = \frac{h}{p} \tag{10.5.1}$$

which is known as the *de Broglie wavelength*. According to this equation, *any* particle having a momentum  $p$  has an associated wavelength  $\lambda = h/p$ . Note that the momentum of a photon is entirely relativistic whereas

for a “normal” particle there is a nonzero rest mass as well as a relativistic mass which both contribute to the momentum. Unless particles are traveling near the speed of light, the relativistic mass is very small and therefore contributes negligibly to the momentum.

Interestingly (and potentially obviously for the skeptic), de Broglie didn’t just grab this relation out of thin air. In fact, he developed this theory around the time Einstein was developing the general theory of relativity, which indicated that a photon has a *relativistic mass*. A relativistic mass, in contrast to an *invariant mass* or *rest mass*, is dependent on the velocity with which the particle travels relative to an observer. The relativistic mass of a photon is related to its energy by

$$E = mc^2 \quad (10.5.2)$$

Now we can invoke two, already established results. The first is the result from classical physics that a wave’s velocity is the product of its frequency and wavelength, namely,  $c = \lambda\nu$  for a photon. Additionally, recall Planck’s relation  $E = h\nu$  for the quantization of energy. Then, using Equation (10.5.2), we have that

$$\begin{aligned} E = mc^2 &= h\nu \\ \frac{c}{\nu} &= \frac{h}{mc} \\ \frac{\lambda\nu}{\nu} &= \frac{h}{p} \\ \lambda &= \frac{h}{p} \end{aligned}$$

which is exactly the de Broglie relation. In the second step, note we used the fact that the momentum of a photon is given by  $p = mc$ .

This result was critical in the development of quantum mechanics because it showed that particles exhibit wave-like behavior. If this were the case, there must be a wave equation that relates the spatial and time dependencies of the wave amplitude for the (wave-like) particle. We could think of this relationship as the quantum analog to Newton’s laws of motion.

## 10.6 The Davisson–Germer Experiment

The Davisson–Germer experiment confirmed de Broglie’s particle of wave-particle duality by illustrating the diffraction of electrons scattered by the surface of nickel crystal. The impetus for this experiment was in part due to the success of illustrating the wave-like nature of X-rays through X-ray scattering experiments.

The setup for this experiment involved firing electrons from a heated filament and accelerating them through a voltage before allowing them to strike the surface of solid nickel. An electron detector was positioned on a moving platform so that it could observe electrons at myriad different diffraction angles. Surprisingly (or unsurprisingly, to those who subscribed to the idea of energy quantization at the time), the scattered beam exhibited a diffraction pattern representative of a wave, confirming the idea of wave-particle duality.

## 10.7 Bohr Model of the Hydrogen Atom

Following Rutherford’s discovery of the structure of an atom, containing a dense, positively charged core with orbiting electrons, the picture of atomic theory became inconsistent with electrodynamic theory and Maxwell’s equations. According to classical mechanics, an electron orbiting the nucleus is constantly accelerating and must therefore radiate away energy until spiraling into the nucleus. To explain this phenomenon required experimental observations followed by quantitative analysis of the results.

Attaining spectral data for different atoms was already possible using a gas discharge tube, a glass tube with metal electrodes on either end to send electrons through it. The container was partially filled with some

type of gas and a generator was turned on to create a current across the tube. Unsurprisingly, the emission spectra of different gasses were all different, however, all of them were *discrete spectra*, meaning they contained only discrete, individual wavelengths. Although this stood in contrast to the prediction of classical mechanics, in the context of Einstein's postulates regarding the quantization of light, these results could be rationalized.

Before Einstein, however, scientists used experimental observation to derive a simple relationship to explain all of the frequencies that appeared on the hydrogen emission spectrum,

$$\tilde{\nu} = \frac{1}{\lambda} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad n_2 > n_1 \quad (10.7.1)$$

where  $\tilde{\nu} = 1/\lambda$  is the wavenumber, typically measured as inverse centimeters, and  $R_H = 109677.581 \text{ cm}^{-1}$  is the *Rydberg constant*. This relationship was only derived after Bohr introduced his model of the atom.

Now, using Einstein's postulates, Niels Bohr put forth a new model of the atom which incorporated quantization to Rutherford's model:

1. The electrons in an atom can exist only in certain allowed orbits.
2. Atomic energies are quantized such that each arrangement of electrons in an atom has a discrete, well-defined energy.
3. An electron can undergo a transition from one energy level to another by emitting or absorbing a photon whose energy is exactly equal to the energy difference between the two energy levels.
4. Electrons can also transition between energy levels by absorbing energy from a collision with another electron or atom.

There are numerous important implications from Bohr's model of the atom:

1. *Matter is stable.* An atom in its ground state has no states of lower energy to jump to and can therefore remain in the ground state forever.
2. *Atoms emit and absorb a discrete spectrum.* Only those photons whose frequencies match the energy difference between electron energy levels can be emitted or absorbed. Photons of other frequencies cannot be emitted or absorbed without violating energy conservation.
3. *Emission spectra can be produced by collisions.* In a gas discharge tube, the current-carrying electrons moving through the tube occasionally collide with the atoms allowing for a transfer of energy. Once the atom is in an excited state, it can emit photons of light as it transitions back down to the ground state.
4. *Each element in the periodic table has a unique spectrum.* The energies of the ground state, first excited state, second excited state, etc., are different for different elements which have a different number of electrons. States with different energies emit and absorb photons of different wavelengths.

To arrive at this model of the atom in the first place Bohr had to make assumptions using wave-particle duality. Considering a hydrogen atom, the Rutherford model states that an electron revolves around the nucleus in a circular orbit. Bohr assumed that the Coulombic attraction to the nucleus was directly equal to the centripetal force that opposed the attraction, in accordance with classical mechanics,

$$\frac{q_e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r} \quad (10.7.2)$$

where  $q_e$  is the charge of an electron,  $r$  is the radius of the orbit,  $m_e$  is the mass of the electron, and  $v$  is the its linear velocity. Equation (10.7.2) places a constraint on the motion of the electron. The velocity  $v$  and radius  $r$  *must* satisfy this relationship in order for the particle to move in a circular orbit. In fact, a similar derivation could be used for any object orbiting a large mass, such as a satellite orbiting the earth. Next, Bohr introduced wave-particle duality by assuming the electron had the de Broglie wavelength  $\lambda = h/p$ . Additionally,



using energy quantization, Bohr further assumed that the length of an orbit had to be an integer multiple of wavelengths such that

$$2\pi r = n\lambda = \frac{nh}{p}, \quad n = 1, 2, 3 \dots \quad (10.7.3)$$

which affords the condition

$$\begin{aligned} 2\pi r &= \frac{nh}{m_e v} \\ m_e v r &= n\hbar, \quad n = 1, 2, 3 \dots \end{aligned} \quad (10.7.4)$$

where  $\hbar = h/2\pi$  is the reduced Planck's constant.

Here, I'll make a brief aside. For any particle in motion, whether it's an electron, a tennis ball, or a planet, the angular momentum  $L$  is given by

$$L = mvr$$

where  $m$  is the mass of the object,  $v$  is its velocity, and  $r$  is its radius. Recall that the angular momentum of *orbital motion* is always conserved because the centripetal force keeping it in orbit is directed exactly at the center of the object and therefore does not exert a torque. So, what role does angular momentum play in our analysis of the hydrogen atom? Well, if we consider Equation (10.7.4), it's clear to see that

$$L = n\hbar, \quad n = 1, 2, 3 \dots$$

and therefore the angular momentum of an orbiting electron is quantized. In particular, it must be an integer multiple of the reduced Planck constant. The quantization of angular momentum is a direct consequence of the wave-like behavior of electrons and we'll come to see that it will lead to the idea of electron shells. Okay, back to Bohr's model of the hydrogen atom.

The rationale for the assumption of integer-multiple wavelengths is intuitive yet far from obvious. As shown in Figure 10.6, Bohr reasoned that unless the orbit length is an integer number of wavelengths, the wave will destructively interfere with itself and the amplitude will decrease to zero in a few orbits. Another way of looking at why the orbit length must consist of an integer number of wavelengths is to reason that the electron must establish a standing wave along the orbit. Altogether, the assertion that there is a stable orbit for the electron in the Rutherford model goes entirely beyond classical physics. Equations (10.7.2) and (10.7.4) simultaneously place two different constraints on the velocity and radius of the orbiting electron due to wave-particle duality.

We can use Equation (10.7.4) to find an expression for the velocity of the electron and substitute into Equation (10.7.2) to find an equation for the radius of the electron orbit as follows:

$$\begin{aligned} \frac{q_e^2}{4\pi\epsilon_0 r^2} &= \frac{m_e(n\hbar/m_e r)^2}{r} \\ r_n &= \frac{4\pi\epsilon_0 \hbar^2}{m_e q_e^2} n^2, \quad n = 1, 2, 3 \dots \end{aligned} \quad (10.7.5)$$

The subscript  $n$  indicates that the radius of the orbit is dependent on the integer  $n$ . Notice that the right-hand side of this equation, aside from  $n^2$ , is a collection of constants. So, we can define the *Bohr radius*,  $a_B$ , as

$$a_B = \frac{4\pi\epsilon_0 \hbar^2}{m_e q_e^2} \approx 5.292 \times 10^{-11} \text{ m} = 0.5292 \text{ \AA} \quad (10.7.6)$$

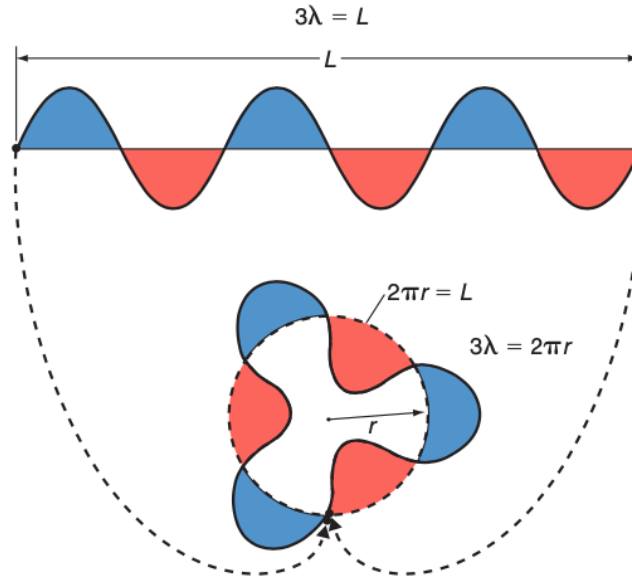


Figure 10.6: A wave traveling in a circular orbit with an integer number of wavelengths. Otherwise, the wave would cancel itself out and be destroyed.

which affords an expression for the radius of an orbiting electron in a hydrogen atom as

$$r_n = n^2 a_B, \quad n = 1, 2, 3 \dots \quad (10.7.7)$$

From Equation (10.7.5) we can see clearly how an electron can have only discrete values for orbital radii, each corresponding to a discrete value of  $n$ . In fact, we can show that the discrete set of orbit radii give rise to a discrete set of energy levels as well.

Note that the total energy of an electron is the sum of its kinetic and potential energy,

$$E = T + V = \frac{1}{2} m_e v^2 - \frac{q_e^2}{4\pi\epsilon_0 r}$$

where the potential energy is given by the electric potential of the electron and each variable represents the same quantity as previously established. Using Equation (10.7.2) we can eliminate velocity from this equation as follows:

$$E = \frac{1}{2} \left( \frac{q_e^2}{4\pi\epsilon_0 r} \right) - \frac{q_e^2}{4\pi\epsilon_0 r} = -\frac{q_e^2}{8\pi\epsilon_0 r}$$

Finally, we can eliminate the radial orbit  $r$  using Equation (10.7.5) to illustrate the discrete set of energy levels.

$$E = -\frac{q_e^2}{8\pi\epsilon_0} \left( \frac{m_e q_e^2}{4\pi\epsilon_0 n^2 \hbar^2} \right) = -\frac{m_e q_e^4}{8\epsilon_0^2 \hbar^2 n^2}, \quad n = 1, 2, 3 \dots \quad (10.7.8)$$

All energy levels in the set given by Equation (10.7.8) are negative because the zero energy arbitrarily corresponds to a proton and electron at infinite separation. The ground state energy corresponds to  $n = 1$  and is the lowest energy that a hydrogen atom can have (recall that Bohr made these calculations with a hydrogen atom in mind). The key step in the derivation of the allowed energy levels within an atom was recognizing that electrons behave as waves *and* particles. This requirement leads to quantized orbits, affording the characteristic integer  $n$  for each orbit, also known as the *quantum number*.

Before continuing, notice that the energy of an electron decreases as  $E \sim -1/n^2$ . So, as  $n \rightarrow \infty$ , the energy of interaction between an electron and the nucleus decreases to zero. Also, recall from Equation (10.7.5)

that the radius of an electron's orbit increases as  $r_n \sim n^2$ . So, in the Bohr model, the radii of electron orbits are concentric circles. Lastly, using Equations (10.7.4) and (10.7.5) we can show that the velocity of an electron decreases as  $v \sim -1/n$ . So, as the quantum number  $n$  increases, the velocity decreases. Intuitively this should make sense. We've already seen that the energy  $E$  of the electron decreases as  $n$  increases. A large part of that energy is in the form of kinetic energy, which is dependent on velocity (the Coulombic attraction between the nucleus and electrons contribute to  $E$  in the form of potential energy but that won't have an effect on our line of reasoning). Hence, if increasing  $n$  decreases velocity then we'd expect it to decrease energy as well. Everything checks out!

Because the energy of an electron can only have discrete values, the light emitted when an electron relaxes from a higher to a lower energy level (or, from energy level  $n_2$  to  $n_1$ ) is a discretized set of frequencies:

$$\nu_{n_2 \rightarrow n_1} = \frac{m_e q_e^4}{8\epsilon_0^2 h^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad n_2 > n_1 \quad (10.7.9)$$

Equation (10.7.10) is in direct agreement with Equation (10.7.1) and so our derived relationship agrees with the empirical formula. Note that  $\nu$  is the frequency and is related to the wavenumber  $\tilde{\nu}$  by  $\nu = c\tilde{\nu}$  where  $c$  is the speed of light so that the Rydberg constant can be expressed as

$$R_H = \frac{m_e q_e^4}{8\epsilon_0^2 h^3 c}$$

Although the Bohr model predicts the absorption and emission frequencies observed in the hydrogen atom, it does not give quantitative agreement with spectra observed for atoms containing more than one electron. Though, this result should make sense. For one thing, other elements in the periodic table have more positive charges in their nuclei and correspondingly more electrons. Moreover, the interaction between many electrons introduces complexity to our analysis of these systems.

Also, the Bohr model is fundamentally incorrect because it assumes that both the position and momentum of an electron within an atom can be known. However, by the uncertainty principle (to be discussed more later) this is impossible.

### 10.7.1 The Line Series of Hydrogen

Because the emission spectra of atoms consist of only certain discrete frequencies, they are often referred to as *line spectra*. For hydrogen, the first elucidated series of line spectra was a massive step toward determining the electronic structure of atoms. The most common series of line spectra are the *Balmer series* and *Lyman series*, while others such as the Paschen series, Brackett series, and Pfund series all supported the Bohr model of the hydrogen atom through empirical results.

With a new formula for determining the frequency of emitted electrons in Equation (10.7.10) through the use of energy quantization, line series could be determined by fixing the energy state to which the electrons relaxed while measuring the frequency of light given off as electrons were excited to different high energy states. Typically, spectroscopists use wave numbers to measure frequencies of emitted electrons, given by  $\tilde{\nu} = 1/\lambda$ , as noted above in the discussion about the Rydberg constant. To measure the wave number of light given off, we'll use Equation (10.7.1):

$$\tilde{\nu}_{n_2 \rightarrow n_1} = R_H \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad n_2 > n_1 \quad (10.7.10)$$

The *Balmer series* is defined as the set of frequencies that arise from electron excitations from the  $n = 2$  energy level to the  $n = 3, 4, 5 \dots$  so that it can be written as

$$\tilde{\nu}_{n_2 \rightarrow 2} = R_H \left( \frac{1}{4} - \frac{1}{n_2^2} \right), \quad n_2 = 3, 4, 5 \dots \quad (10.7.11)$$

Note that the observed frequencies in this set fall within the visible light spectrum. Similarly, the *Lyman series* is defined as the set of frequencies that arise from electron excitations from the  $n = 1$  energy level to all those above,

$$\tilde{\nu}_{n_2 \rightarrow 1} = R_H \left( 1 - \frac{1}{n_2^2} \right), \quad n_2 = 2, 3, 4, \dots \quad (10.7.12)$$

In contrast to the Balmer series, the frequencies in the Lyman series fall within the ultraviolet spectrum.

## 10.8 Classical versus Quantum Mechanics

It's important to recognize that classical mechanics and quantum mechanics are not competing theories but instead different ways of describing the world. In some cases classical mechanics work better and in others you'd be better suited to use quantum mechanics. As an example, consider a container filled with hydrogen gas at a standard conditions. The origin of the pressure in the container arises from rapid collisions between atoms and the walls of the container. As we know from experience, classical mechanics gives a perfectly valid description of the pressure. In contrast, if we pass ultraviolet light through the gas and ask how much energy is taken up by an  $H_2$  molecule, a quantum mechanical description is necessary.

The dawn of quantum mechanics introduced the idea that particles and waves are not separate entities. So, determining if a system requires a classical description or a quantum description is equivalent to determining if the system can be treated as a particle (or a collection of particles) or if it could be described by a wave, respectively. Two criteria are used to make this distinction: the magnitude of the wavelength of the particle relative to the dimensions of the problem and the degree to which the allowed energies of the system form a continuous spectrum.

A good starting point is to consider a diffraction experiment. If a wave of wavelength  $\lambda$  passes through a slit of width  $a$  and  $\lambda \ll a$  then a classical description is fine and we can use ray tracing (in the context of this diffraction experiment, that is) for the experiment. Diffraction is observed only when the size of the slit is comparable to the wavelength of light so that  $\lambda \approx a$ . Determining the wavelength of any particle can be done using the de Broglie relation, Equation (10.5.1). The de Broglie relation deals with momentum so the wave behavior of massive objects does not manifest itself. Additionally, there is no sharp boundary for being able to describe an object as a particle or a wave; The degree to which each of these properties is exhibited flows smoothly from one extreme to the other.

The second criterion for determining the type of mechanics necessary for a situation is based on the energy spectrum of the system. Classical physics deals with a *continuous* energy spectrum whereas quantum physics deals with a *discrete* energy spectrum. In practice, this distinction may be intuitive at times but to make it more quantitative we can consider the Boltzmann distribution from statistical mechanics.

Before we do that, recall the *Maxwell*–Boltzmann distribution, which is a little bit different from the Boltzmann distribution. If we consider an monoatomic gas of mass  $m$  at temperature  $T$ , the Maxwell–Boltzmann distribution states that the probability of finding an atom at velocity  $v$  is given by

$$P_T(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{1}{2} \left( \frac{mv^2}{k_B T} \right)}, \quad -\infty < v < \infty \quad (10.8.1)$$

We can rewrite this expression assuming that the gas is ideal so that the energy  $\varepsilon$  of a particle is completely kinetic energy. Moreover, if we take a ratio of any two probabilities, say, the ratio of probabilities for atoms at velocities  $v_i$  and  $v_j$ , the constants out front go away and our lives become a bit simpler:

$$\frac{P_i}{P_j} = \frac{v_i^2}{v_j^2} e^{-(\varepsilon_i - \varepsilon_j)/k_B T} \quad (10.8.2)$$

Most generally, if we assume that the probability of attaining any velocity is *a priori* equally likely then we

can rewrite this distribution as

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-\Delta\varepsilon/k_B T} \quad (10.8.3)$$

where  $\Delta\varepsilon = \varepsilon_i - \varepsilon_j$  is the difference in energy levels,  $n_i$  and  $n_j$  are the number of particles in states  $i$  and  $j$ , respectively, and  $g_i$  and  $g_j$  are the degeneracies of the respective states. This is one way to write the *Boltzmann distribution*. In any of the Equations (10.8.1) through (10.8.3) we see that the probability of an atom having an energy  $\varepsilon$  falls off exponentially as  $\varepsilon$  increases. Another aspect of the distribution which is clear (and is very clear from a study of statistical mechanics) is the importance of  $k_B T$ , the average energy that an atom will have at temperature  $T$ . Thus, we can understand the exponential term of Equation (10.8.3) as telling us that larger temperatures cause the ratio of  $n_i/n_j$  to go to 1, or that the deviation in energy states decreases.

What about quantum mechanics? Great question. If  $k_B T$  is small compared to the spacing of allowed energies  $\Delta\varepsilon$ , that is,  $k_B T \ll \Delta\varepsilon$ , classical and quantum mechanics will give much different results for the energy spectrum. To make this result more clear, consider a system of ideal atoms with only translational freedom in three-dimensions. The kinetic energy of each atom will be  $\frac{3}{2}k_B T$  by equipartition. Moreover, suppose that this system has very large gaps between allowed energies such that in order to excite the system from energy level  $n = 1$  to  $n = 2$ , we require an input of  $k_B T \times 10^{100}$  J. As we add particles, however, we're only adding  $\frac{3}{2}k_B T$  J per particle and would therefore require an immense amount of particles (or just any form of energy) to allow the system to reach an excited state. Hence, we require a quantum mechanical description of the system.

Inversely, if  $k_B T$  is much larger than the difference between the allowed energy states, classical and quantum mechanics will give the same result for the relative number of particles in each energy state. That is, they both provide an adequate description of the system. To reinforce this idea, consider a system of 1000 particles which can occupy one of two energy states,  $\varepsilon_1$  and  $\varepsilon_2$ , with  $\varepsilon_2 > \varepsilon_1$ . The difference in the energy levels is denoted  $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$  and further suppose that the degeneracies of the energy levels are the same. If we allow  $n_1$  and  $n_2$  to denote the number of particles in the first and second energy levels, respectively, from the Boltzmann distribution we have that

$$\frac{n_2}{n_1} = e^{-\Delta\varepsilon/k_B T}$$

with  $n_1 + n_2 = 1000$ . Solving this system<sup>8</sup> for  $n_2$  and  $n_1$  as a function of energy and temperature affords

$$n_2 = \frac{1000e^{-\Delta\varepsilon/k_B T}}{1 + e^{-\Delta\varepsilon/k_B T}}, \quad n_1 = \frac{1000}{1 + e^{-\Delta\varepsilon/k_B T}}$$

Figure 10.7 presents a plot of  $n_1$  and  $n_2$  as a function of  $k_B T/\Delta\varepsilon$ . Now, the relationship between the difference in energy levels and  $k_B T$  becomes more clear. When  $k_B T/\Delta\varepsilon$  is small (or, when  $\Delta\varepsilon/k_B T$  is large), the vast majority of particles are in the lower energy state  $\varepsilon_1$ . Stated in another way, when a system requires a quantum mechanical description because the difference in allowed energies exceeds  $k_B T$ , the number of particles in the lower energy state will dominate. Similarly, either a classical or quantum mechanical description will suffice for a system when the difference in allowed energies is negligible compared to  $k_B T$ .

### 10.8.1 The Correspondence Principle

One way to understand the convergence between classical and quantum mechanical descriptions of a system is to consider the measurement process. Any measurement on an observable quantity for a system has a certain resolution that averages data over the resolution range. For example, when we use an oscilloscope to measure the frequency of a wave, the resolution of the oscilloscope is the smallest increment in time it can detect, whether it be seconds, milliseconds, nanoseconds, etc. Anything beyond the smallest increment is averaged and

<sup>8</sup>Although a solution for the number of particles presented here relies on the Boltzmann distribution, an equally reliable way of reaching this conclusion could have been done using statistical mechanics and finding the partition function for the system.

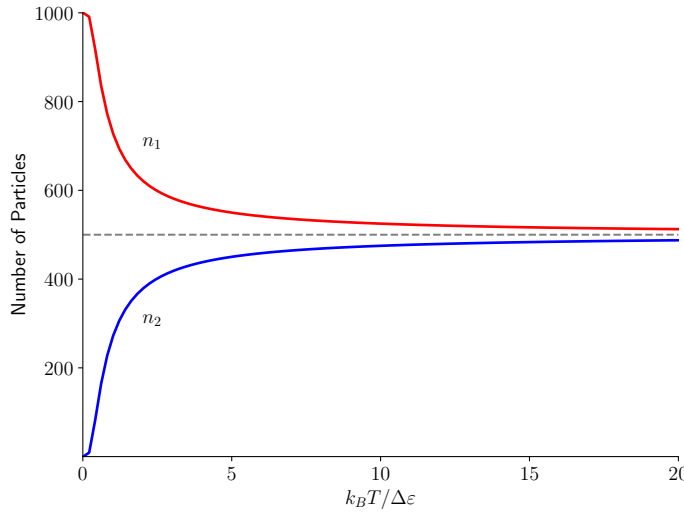


Figure 10.7: Plot of number of particles in either energy level  $\varepsilon_1$  or  $\varepsilon_2$  with  $\varepsilon_2 > \varepsilon_1$  as a function of the ratio  $k_B T / \Delta\varepsilon$ .

added to the final observed frequency. From the perspective of classical mechanics, our resolution of quantum mechanical states is very poor so that energy fluctuations on the order of  $k_B T$  are unnoticeable. Then, as the energy of the system increases, energy *fluctuations* increase until they become noticeable and the “resolution” of classical mechanics may predict the system’s behavior. Hence the convergence of quantum mechanics with classical mechanics as the energy of a system increases, or, as the difference in allowed energy decreases.

When we study the Schrödinger equation we’ll see that the energy of a particle in a one-dimensional box at some energy level  $n$  is given by  $E_n = h^2 n^2 / 8ma^2$  for  $n = 1, 2, 3 \dots$  where  $m$  is the mass of the particle,  $a$  is the length of the box, and  $h$  is Planck’s constant. We may consider the energy spacing between levels by looking at the ratio  $(E_{n+1} - E_n) / E_n$ , which can be thought of as the factor by which the energy increases from level  $n$  to  $n + 1$ .

$$\frac{E_{n+1} - E_n}{E_n} = \frac{h^2(n+1)^2/8ma^2 - h^2n^2/8ma^2}{h^2n^2/8ma^2} = \frac{(n+1)^2 - n^2}{n^2} = \frac{2n+1}{n^2}$$

In the limit that  $n \rightarrow \infty$ , this ratio approaches zero so that the energy spacing between levels approaches zero. This result and all other ways of saying that classical and quantum mechanics converge for large enough energies are part of the general result known as the *correspondence principle*.

## CHAPTER

# 11

# THE QUANTUM MECHANICAL FRAMEWORK

*All models are wrong, but some are useful.*

- George E.P. Box

The quantum mechanical framework provides the necessary equations and postulates necessary to explore quantum models and phenomena. We'll start by introducing the Schrödinger Equation, the quantum mechanical analog to Newton's second law of motion,  $F = ma$ . This equation will serve as a basic introduction to operators and motivation to define the *quantum mechanical postulates*, which can be thought of as necessary conditions for any allowable quantum mechanical state.

Together, the Schrödinger equation and the quantum mechanical postulates will allow us to explore the different types of particle motion—translational, vibrational, rotational, and electronic—and their relevant models.

## 11.1 The Schrödinger Equation

A year following de Broglie's suggestion that matter may have wave-like properties, Erwin Schrödinger discovered the law of quantum mechanics, commonly referred to as the *Schrödinger equation*. It is the law of quantum mechanics in the same way that Newton's laws are the laws of classical mechanics. It gives the evolution over time of a *wave function*, the quantum-mechanical characterization of a system.

It's important to note that the Schrödinger equation isn't necessarily "derived". Although we can derive the classical wave equation (Appendix ??) and although I'll present a formulation of the Schrödinger equation from that, we rely on de Broglie's relation between wavelength and momentum, an equation which in and of itself seemingly appeared out of thin air. In fact, in his lectures on physics Richard Feynman opined that

We do not intend to have you think we have derived the Schrödinger equation but only wish to show you one way of thinking about it. When Schrödinger first wrote it down, he gave a kind of derivation based on some heuristic arguments and some brilliant intuitive guesses. Some of the arguments he used were even false, but that does not matter; the only important thing is that the

ultimate equation gives a correct description of nature... Where did we get that from? Nowhere. It's not possible to derive it from anything you know. It came out of the mind of Schrödinger, invented in his struggle to find an understanding of the experimental observations of the real world.

Nevertheless, we may use the classical wave equation to arrive at Schrödinger's result. To begin, suppose that we have a standing wave  $\Psi(x, t) = \psi(x) \cos(\omega t)$ . Recall the classical wave equation,

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \quad (11.1.1)$$

a derivation for which can be found in Appendix ???. Substituting  $\Psi(x, t)$  for the wave function  $y$  we have that

$$\begin{aligned} \frac{\partial^2 \Psi(x, t)}{\partial x^2} &= \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2} \\ \frac{\partial^2}{\partial x^2} [\psi(x) \cos(\omega t)] &= \frac{1}{v^2} \frac{\partial^2}{\partial t^2} [\psi(x) \cos(\omega t)] \\ \cos(\omega t) \frac{\partial^2 \psi(x)}{\partial x^2} &= \frac{\omega^2}{v^2} (-\psi(x) \cos(\omega t)) \\ \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{\omega^2}{v^2} \psi(x) &= 0 \end{aligned} \quad (11.1.2)$$

Recall that the angular frequency  $\omega$  is related to the linear frequency  $\nu$  by  $\omega = 2\pi\nu$  and that the velocity  $v$  of the wave is related to the frequency by  $v = \lambda\nu$ . After a little bit of algebraic gymnastics we can rewrite Equation (11.1.2) as

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \psi(x) = 0 \quad (11.1.3)$$

To satisfy the properties of quantum systems we now introduce the de Broglie relation to the constraints on this wave. By that I mean we must relate the wavelength to the wave's momentum. Before we make this substitution, however, note that we can relate the momentum of a wave to its energy by

$$\begin{aligned} \frac{1}{2}mv^2 &= \frac{p^2}{2m} = E - V \\ p &= \sqrt{2m(E - V)} \end{aligned} \quad (11.1.4)$$

where  $E$  represents the total energy of the wave,  $V$  represents its potential energy, and therefore  $E - V$  represents its kinetic energy by the law of conservation of energy. Using de Broglie's relation we have that

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E - V)}}$$

and Equation (11.1.3) can be expressed as

$$\begin{aligned} \frac{\partial^2 \psi(x)}{\partial x^2} + 4\pi^2 \left( \frac{\sqrt{2m(E - V)}}{h} \right)^2 \psi(x) &= 0 \\ \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m(E - V)}{\hbar^2} \psi(x) &= 0 \\ \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + (E - V) \psi(x) &= 0 \\ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V \psi(x) &= E \psi(x) \end{aligned}$$

Oftentimes the potential energy of a system changes with position<sup>1</sup> and so we write  $V(x)$ . This affords us the

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<sup>1</sup>This is fairly intuitive. If we are dealing with charges (which, last I checked, electrons and protons have charges) there are electric fields inherent in the system and with each electric field is an electric potential which defines the potential energy of the system.



one-dimensional *time-independent Schrödinger equation*, written

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E\psi(x) \quad (11.1.5)$$

This is the fundamental equation used to study stationary states of quantum mechanical systems. Using the classical wave equation in three dimensions instead of just one we can derive a similar relationship for the Schrödinger equation, generalized to three-dimensional space,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (11.1.6)$$

where  $\vec{r} = (x, y, z)$ . Above I took advantage of the *Laplacian operator*,  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  to simplify notation. Refer to Appendix ?? for discussion on waves in more than one dimension and the Laplacian operator.

The generalization of the Schrödinger equation to three dimensions illustrates its similarity to the classical equation for particle energy, derived from *Hamiltonian mechanics*:

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x, y, z) = E \quad (11.1.7)$$

where  $p_x$ ,  $p_y$ , and  $p_z$ , are the momenta in the  $x$ ,  $y$ , and  $z$  directions, respectively. For this reason, the Schrödinger equation is oftentimes written as

$$\hat{H}\psi = E\psi \quad (11.1.8)$$

where  $\hat{H}$  is the *Hamiltonian operator* (or the *total energy operator*), and  $\psi$  is the spatial component of the wave function as defined previously.

There is an analogous quantum mechanical form of the *time-dependent* classical wave equation, referred to as the *time-dependent Schrödinger equation*, written

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t)\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (11.1.9)$$

with an analogous three-dimensional form,

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t)\Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} \quad (11.1.10)$$

No matter which of the Equations (11.1.5) through (11.1.10) you consider, there is an intuitive interpretation of Schrödinger's Equation which should be kept in mind. The Hamiltonian operator  $\hat{H}$  has two parts: the  $\nabla^2$  part represents the “wiggleness” of the wave function while  $V$  simply represents the potential energy of the system at various points in space. The Schrödinger equation requires both of these parts to counterbalance each other at every point in space so that they always combine to give the same value of the total energy  $E$ .

### 11.1.1 Quantum Mechanical Operators and Observables

To measure any observable quantity, such as energy, momentum, or position, in quantum mechanics we require an operator, unlike in classical mechanics where those may be measurable. One common operator is the Hamiltonian that we see in the (one-dimensional) Schrödinger equation,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

Simply put, an operator is a way of writing instructions for whatever follows. I could write  $\hat{B}f(x)$  where  $\hat{B}$  implies

- Take the square root of the function

- Set the function equal to 4
- Do laundry
- Take the square root of the function again

and that would be a valid operator. A more relevant example might be the differentiation and integration operators that we are familiar with.

In quantum mechanics we'll deal only with linear operators, those which satisfy the relation

$$\hat{A}[c_1 f(x) + c_2 g(x)] = c_1 \hat{A}f(x) + c_2 \hat{A}g(x)$$

where  $c_1$  and  $c_2$  are constants and  $f(x)$  and  $g(x)$  are some functions. Common linear operators are differentiation and integration, as mentioned previously. In contrast, the “square” operator is *not* linear. If we let  $\hat{S}$  be the operator telling us to square an expression,

$$\hat{S}[f(x) + g(x)] = f^2(x) + 2f(x)g(x) + g^2(x) \neq f^2(x) + g^2(x)$$

and therefore  $\hat{S}[f(x) + g(x)] \neq \hat{S}f(x) + \hat{S}g(x)$ .

### 11.1.2 The Schrödinger Equation as an Eigenvalue Equation

The Schrödinger equation is an example of an *eigenvalue equation*. An eigenvalue equation is any relationship of the form

$$\hat{A}f_i = \lambda_i f_i \tag{11.1.11}$$

where  $\hat{A}$  is an operator,  $f_i$  is a function, referred to as the *eigenfunction*, and  $\lambda_i$  is some scalar constant, referred to as the *eigenvalue*. Typically an operator can have an infinite number of eigenfunctions so that the subscript  $i$  is used to denote which eigenfunction corresponds to which eigenvalue. In the case of Equation (11.1.8), the Hamiltonian operator  $\hat{H}$  is the quantum mechanical operator that returns the total energy  $E$  which is the eigenvalue of the equation. Also, the wave function  $\psi$  is the eigenfunction.

The fact that Schrödinger's equation is an eigenvalue equation should agree with your intuition. As we'll come to see, the wave function of a particle *completely defines that particle*: everything about the particle's position, linear and angular momentums, kinetic and potential energies, etc., can be determined from the wave function. As we operate on a wave function  $\Psi$ , then, we're only concerned with that particular  $\Psi$ . If  $\Psi$  were to change at all then we're no longer studying the particular particle we concerned ourselves with initially. Hence, when we operate on a wave function, we're only concerned with those operators *which return the same wave function* so that we know we're studying the same particle. This is a rationale behind the Schrödinger equation being an eigenvalue equation.

## 11.2 The Quantum Mechanical Postulates

Quantum mechanical postulates formalize the conjectures made by scientists on the behavior of matter at a quantum level. Establishing these postulates is similar to setting up a series of axioms and then logically deducing the consequences of those axioms. Just as the basic definitions of knot theory had to be elucidated before Lisa Piccirillo could solve the Conway knot problem, quantum mechanical postulates must be established before we can go on to prove more impactful results. Energy quantization, confinement, and uncertainty may all be explained with a properly chosen set of postulates.

### 11.2.1 The Physical Interpretation of a Wave Function is Probability

Our first postulate of quantum mechanics can be stated as follows:

*The state of a quantum mechanical particle is defined completely by a wave function  $\Psi(\vec{x}, t)$ . The probability that the particle will be found at time  $t_0$  in a spatial interval of width  $dx$  centered at  $\vec{x}_0$  is given by*

$$\Psi(\vec{x}_0, t_0)^* \Psi(\vec{x}_0, t_0) dx \quad (11.2.1)$$

The first point, that a quantum mechanical particle is *completely defined by the wave function*, cannot be understated. Recall from classical mechanics that our goal in any situation is ultimately to model the trajectory of a system as a function of the time. That is, we're looking for some function  $x(t)$  which tells us the position of a particle at any time  $t$  (with only one spatial coordinate considered to simplify notation). From this, we can deduce any quantity we want:

- The velocity of the particle is given by  $v = \frac{dx}{dt}$  and the acceleration is given by  $a = \frac{d^2x}{dt^2}$ . Moreover, the momentum can be found as  $p = m \frac{dx}{dt}$ .
- The force acting on the particle is given by  $F = m \frac{d^2x}{dt^2}$ .
- The kinetic energy can be found as  $T = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2$
- The gravitational, coulombic (assuming charges are present and known), and spring potential energies can be found as

$$U_{\text{gravity}} = mgx, \quad U_{\text{coulombic}} = \frac{kQ_1Q_2}{x}, \quad U_{\text{spring}} = \frac{1}{2}kx^2$$

The list may go on and on, though, I feel like my point is made. Similarly to classical mechanics, any measurable quantity or observable of a system can be obtained from the wave function. As we'll see later, these observables can be deduced from the wave function through the use of operators.

The association of the wave function with a probability is sometimes referred to as *Born's rule*, formulated by physicist Max Born in 1926. This association places an important requirement on the wave function: *normalization*. Inherent in some wave function being defined as a probability distribution is the fact that it must integrate to zero over all positions. That is,

$$\int_{\text{all } x} \Psi^*(x, t) \Psi(x, t) dx = 1 \quad (11.2.2)$$

In addition to this requirement are subsequent conditions the wave function must satisfy. For any wave function  $\Psi(x, t)$ ,

- It must be *single-valued*. That is, for any spatial coordinate  $x_0$ ,  $\Psi(x_0, t)$  must return only one scalar value. If this were not the case, a particle would have more than one probability of being in a position in space. A more mathematically rigorous way of describing this condition is to say that  $\Psi$  must be *injective* or *one-to-one*.
- It must be twice-continuously differentiable. In other words, the second derivative of  $\Psi(x, t)$  must exist, otherwise, the Schrödinger equation could not be setup.
- It may not have an infinite amplitude over a finite interval. Otherwise,  $|\Psi(x, t)|^2$  could not be properly normalized. For example, the function  $\psi(x) = e^{-x}$  on  $x \in [-\infty, \infty]$  has an infinite amplitude as  $x \rightarrow -\infty$  and therefore cannot act as a wave function. In contrast, the wave function  $\psi(x) = e^{-x}$  on  $x \in [0, \infty]$  has a finite amplitude over the entire amplitude and so it can be properly normalized and is therefore a wave function.

### 11.2.2 All Observables Have a Corresponding Operator

The second postulate of quantum mechanics we'll concern ourselves with can be stated as follows:

*For every measurable property of a system there exists a corresponding linear, Hermitian operator in quantum mechanics.*

Suppose, for example, that we measured the momentum of a ball rolling down a hill. Further suppose that we wanted to perform this same experiment at a quantum mechanical-level, modeling an electron rolling down a really small hill. In classical physics we could measure the momentum of the ball exactly, however, in quantum mechanics we could not (for a myriad of reasons). Instead, we use quantum mechanical operators to determine these observables. Amazingly, if the classical formula for a physical quantity is expressed in terms of, say, momentum, we can create the corresponding quantum mechanical operator by replacing every instance of the momentum with the momentum operator,  $\hat{p}$ . As an example, consider the classical kinetic energy formula,  $T = p^2/2m$ . To create the corresponding operator in quantum mechanics we can simply replace the momentum by its operator. Hence,

$$\hat{T} = \frac{1}{2m} \left( -i\hbar \frac{\partial}{\partial x} \right)^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

is the kinetic energy operator. Of course, this is assuming we knew the momentum operator. Now we'll go onto show where some of these operators come from.

We've already been introduced to one of these operators, the Hamiltonian operator,  $\hat{H}$ , which returns the total energy of the system. Just as we could measure the total energy of a classical system by considering an object's position and momentum, we can measure the total energy of a quantum system by operating on the wave function with  $\hat{H}$ .

Interestingly, we can “derive” the other important quantum mechanical operators only knowing the form of  $\hat{H}$ . Recall that the Hamiltonian is written

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

and represents the total energy of the system. By definition,  $V(x)$  represents the potential energy of the system and so we can immediately deduce two more quantum mechanical operators, those for the kinetic and potential energies:

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (11.2.3)$$

$$\hat{V} = V(x) \quad (11.2.4)$$

Above it should be noted that both of these operators are represented using one spatial coordinate  $x$ . In three dimensions, the result extends simply by exchanging  $x$  for  $y$  or  $z$  for the  $y$ - and  $z$ -directions, respectively.

With an operator for the kinetic energy we can also find the operator for a particle's momentum. Recall that kinetic energy is related to momentum by  $T = p^2/2m$  which affords the relationship  $p = \sqrt{2mT}$ . Thus, the momentum operator is given by

$$\hat{p} = \sqrt{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}} = -i\hbar \frac{\partial}{\partial x} \quad (11.2.5)$$

Above it's probably clear why I put “derive” in quotes earlier. I must be breaking like 15 laws by taking the square root of a second derivative but for now it'll have to do. Table 11.1 illustrates relevant observables and their quantum mechanical operators.

Of interest is the quantum mechanical operator for the angular momentum of a particle. Recall from

Observable	Symbol	Operation (1D)	Operation (3D)
Position	$\hat{x}$	$x$	$(x, y, z)$
Momentum	$\hat{p}$	$-i\hbar \frac{\partial}{\partial x}$	$-i\hbar \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$
Angular Momentum	$\hat{l}_x$	$-i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$	
	$\hat{l}_y$	$-i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$	
	$\hat{l}_z$	$-i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$	
Kinetic Energy	$\hat{T}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$	$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$ $= -\frac{\hbar^2}{2m} \nabla^2$
Potential Energy	$\hat{V}$	$V(x)$	$V(x, y, z)$
Total Energy	$\hat{H}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$	$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z)$ $= -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$

Table 11.1: Observables and their quantum mechanical operators. For those operations which contain only a variable, such as  $\hat{x}$  or  $\hat{V}$ , it is implied that the operation is just multiplication. Also, for the 3D operations which operate with a vector, the result of the operation will also be a vector.

classical mechanics that we define the angular momentum of a particle as

$$\vec{L} = \vec{r} \times \vec{p}$$

where  $\vec{r} = (x, y, z)$  is the particle's position vector,  $\vec{p}$  is the linear momentum vector and  $\vec{L}$  is defined by their cross product. Using quantum mechanical operators in place of the classical vectors  $\vec{L}$ ,  $\vec{r}$ , and  $\vec{p}$ , we have that

$$\begin{aligned} \hat{L} &= \hat{x} \times \hat{p} \\ &= (x, y, z) \times (-i\hbar) \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \\ &= -i\hbar \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix} \\ &= (-i\hbar) \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \hat{i} - (-i\hbar) \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \hat{j} + (-i\hbar) \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \hat{k} \\ &= (\hat{L}_x, \hat{L}_y, \hat{L}_z) \end{aligned}$$

which agrees with the result presented in Table 11.1.

Of note is the fact that all quantum mechanical operators we'll consider in quantum mechanics are considered *Hermitian operators*, or *self-adjoint*. A Hermitian operator is an operator which is equal to its conjugate transpose. As an example, the matrix

$$A = \begin{bmatrix} 1 & -i \\ i & 1 \end{bmatrix}$$

is Hermitian because  $A = (A^*)^T$ . For us, the most immediate consequence of this fact is that we can write

$$\int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi dx = \int_{-\infty}^{\infty} \Psi \hat{A}^* \Psi^* dx \quad (11.2.6)$$

for some wave function  $\Psi(x, t)$  and operator  $\hat{A}$ . Moreover, it can be proven most generally that a Hermitian operator enjoys the property

$$\int_{-\infty}^{\infty} \Psi_m^* \hat{A} \Psi_n dx = \int_{-\infty}^{\infty} \Psi_n \hat{A}^* \Psi_m^* dx \quad (11.2.7)$$

Later when we deduce the average value of quantum mechanical systems this relationship will make our lives easier.

An amazing aspect of Hermitian operators is that they have strictly real eigenvalues. We've already been introduced to a plethora of quantum mechanical operators such as those for position, momentum, and energy, among others. Most of these operators contain complex numbers, however, if the eigenvalues of these operators correspond to observable quantities surely their eigenvalues must be real numbers.

### 11.2.3 Results of Quantum Mechanical Measurements

The third postulate of quantum mechanics we'll concern ourselves with can be stated as follows:

*In any single measurement of the observable that corresponds to an operator  $\hat{A}$ , the only values that will ever be measured are the eigenvalues of  $\hat{A}$ .*

Generally, an operator will have a set of eigenfunctions and eigenvalues, indicated by writing  $\hat{A}\Psi_i = a_i\Psi_i$  for some index  $i$ . Thus, the observables corresponding to  $\hat{A}$  are  $a_1, a_2, a_3, \dots$ . The set of eigenvalues of an operator  $\hat{A}$  is referred to as the *spectrum* of  $\hat{A}$ .

Interestingly, this postulate does not comment on the function which  $\hat{A}$  operates on. That is, operating on some function  $f_i$  to afford  $\hat{A}f_i = \lambda_i f_i$  yields the eigenvalue  $\lambda_i$ , however, we don't need  $f_i$  to be an eigenfunction of  $\hat{A}$ . This is because the eigenfunctions of  $\hat{A}$  form a subset of an infinite number of possible functions which satisfy the requirements of being a wave function.

For a quantum mechanical system, what differences arise when we operate on a function which *is not* an eigenfunction of the operator? Take, for example, the Schrödinger equation,  $\hat{H}\Psi_i = E_i\Psi_i$ . We already know that if the wave function  $\Psi_i$  is an eigenfunction of  $\hat{H}$  then operating on  $\Psi_i$  will return the corresponding energy of the system  $E_i$ . If  $\Psi_i$  were not an eigenfunction of  $\hat{H}$ , although the measured value will still be some eigenvalue of  $\hat{H}$ , the eigenvalue cannot be predicted with certainty. That is,  $\hat{H}\phi_i = E_j\phi_i$  where  $i$  and  $j$  are not necessarily equal.

It's important to keep in mind that we still observe all possible energies  $E_j$  of the system described above. Just because we operate on a function which is not an eigenfunction *does not imply* that we measure an energy which would be otherwise unattainable. That would be violating the laws of quantum mechanics.

### 11.2.4 Expectations of Quantum Mechanical Measurements

The fourth postulate of quantum mechanics we'll concern ourselves with can be stated as follows:

*If the value of an observable quantity  $a$  is measured many times in a system described by the normalized wave function  $\Psi(x, t)$ , the expected value of all these measurements is given by*

$$\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx}{\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx} \quad (11.2.8)$$

If the wave function  $\Psi(x, t)$  is properly normalized then the denominator of Equation (11.2.8) will evaluate to 1. Notice that two cases apply to the wave function  $\Psi(x, t)$  in regard to the operator  $\hat{A}$ :  $\Psi$  *is* or *is not* an eigenfunction of  $\hat{A}$ . Hence, we need to examine each case separately.

Firstly, we'll consider the case where  $\Psi$  is an eigenfunction of  $\hat{A}$ . Then, it must be the case that  $\hat{A}\Psi_i = a_i\Psi_i$  for some scalar  $a_i$ . Then, Equation (11.2.8) becomes

$$\begin{aligned} \langle a \rangle &= \int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx = \int_{-\infty}^{\infty} \Psi^*(x, t) a_i \Psi(x, t) dx \\ &= \int_{-\infty}^{\infty} a_i \Psi^*(x, t) \Psi(x, t) dx \end{aligned} \quad (11.2.9)$$

Here, recall that  $\Psi^*(x, t)\Psi(x, t)dx$  has a probabilistic interpretation so that the Equation (11.2.9) represents a weighted average and is identical to how we may think of averages from a probabilistic standpoint using the law of the unconscious statistician. Furthermore, by normalization we have that all measurements on the system will give the same answer, namely,  $a_i$ .

Now we consider the second case where  $\Psi$  might not be an eigenfunction of the operator  $\hat{A}$ . Recall that since the eigenfunctions of  $\hat{A}$  form a complete set, we can represent  $\Psi$  as a linear combination of them,

$$\Psi(x, t) = b_1\phi_1(x, t) + b_2\phi_2(x, t) + \cdots + b_n\phi_n(x, t) = \sum_{i=1}^n b_i\phi_i(x, t)$$

where  $b_i$  is some scalar coefficient and  $\phi_1, \dots, \phi_n$  are wave functions and are members of the set of eigenfunctions of  $\hat{A}$ . Because we can write  $\Psi$  such that it's normalized, we have that  $\sum b_i^*b_i = 1$ , that is, the coefficients in

the expansion for  $\Psi$  are normalized as well. Substituting these results into Equation (11.2.8),

$$\begin{aligned}\langle a \rangle &= \int_{-\infty}^{\infty} \left( \sum_{i=1}^n b_i^* \phi_i^*(x, t) \right) \hat{A} \left( \sum_{j=1}^n b_j \phi_j(x, t) \right) dx \\ &= \int_{-\infty}^{\infty} \left( \sum_{i=1}^n b_i^* \phi_i^*(x, t) \right) \left( \sum_{j=1}^n a_j b_j \phi_j(x, t) \right) dx \\ &= \sum_{i=1}^n \sum_{j=1}^n a_j b_i^* b_j \int_{-\infty}^{\infty} \phi_i^*(x, t) \phi_j(x, t) dx\end{aligned}$$

This expression is simplified immensely when we recall that the eigenfunctions of an operator form an *orthonormal set* so that the only nonzero terms in the integrand (and summation) above are those for which  $i = j$ . Thus,

$$\langle a \rangle = \sum_{j=1}^n b_j^* a_j b_j = \sum_{j=1}^n |b_j|^2 a_j \quad (11.2.10)$$

where, once again, we observe that the average value of a system is a weighted average. To provide an intermittent concrete example, this equation could be rewritten to represent energies,

$$\langle E \rangle = \sum_{j=1}^n p_j E_j$$

where  $E_j$  is the energy of state  $j$  of the system and  $p(E_j)$  is the probability of observing an energy of  $E_j$ . This provides us with a concrete interpretation of the coefficient  $|b_j|^2$  in Equation (11.2.10): it represents the probability of observing a value of  $a_j$  for some observable  $a$ .

Using the example of energy once more, suppose that a system is in an energy eigenstate  $\psi_1$  so that  $\hat{H}\psi_1 = E_1\psi_1$ . Then, all of the coefficients  $b_j$  are zero, except for  $b_1$  which is equal to 1. Therefore, the probability of observing an energy of  $E_1$  is certain, in accordance with postulate 3.

In any case, whether  $\Psi(x, t)$  is an eigenfunction of  $\hat{A}$  in Equation (11.2.8) or not, we've seen that wave functions and observables for quantum mechanical systems have almost strictly probabilistic interpretations.

As an example, suppose we wanted to determine the average momentum for a free particle of mass  $m$  in two cases, where  $\psi_1(x) = e^{-ikx}$  and where  $\psi_2(x) = \cos(kx)$ . While evaluating these quantities isn't very difficult, their results will offer some valuable discussion. Also, notice that we haven't gone necessarily normalized either of these wave functions so the denominator in Equation (11.2.8) isn't necessarily one.

$$\begin{aligned}\langle p_1 \rangle &= \frac{\int_{-\infty}^{\infty} \psi_1^* \hat{p} \psi_1 dx}{\int_{-\infty}^{\infty} \psi_1^* \psi_1 dx} \\ &= \frac{\int_{-\infty}^{\infty} e^{ikx} \left( -i\hbar \frac{\partial}{\partial x} e^{-ikx} \right) dx}{\int_{-\infty}^{\infty} e^{ikx} e^{-ikx} dx} \\ &= -i\hbar \frac{\int_{-\infty}^{\infty} e^{ikx} (-ik) e^{-ikx} dx}{\int_{-\infty}^{\infty} dx} \\ &= -k\hbar \frac{\int_{-\infty}^{\infty} e^{ikx} e^{-ikx} dx}{\int_{-\infty}^{\infty} dx} \\ &= -k\hbar\end{aligned}$$

We've shown that the average momentum of the wave function  $\psi_1(x) = e^{-ikx}$  is  $\langle p_1 \rangle = -k\hbar$ . Notice that we could still evaluate this quantity even though  $\psi_1(x)$  was not normalized. Now we'll run through the same



calculation with  $\psi_2(x)$ :

$$\begin{aligned}
 \langle p_2 \rangle &= \frac{\int_{-\infty}^{\infty} \psi_2^* \hat{p} \psi_2 dx}{\int_{-\infty}^{\infty} \psi_2^* \psi_2 dx} \\
 &= \frac{\int_{-\infty}^{\infty} \cos(kx) \left( -i\hbar \frac{\partial}{\partial x} \cos(kx) \right) dx}{\int_{-\infty}^{\infty} \cos^2(kx) dx} \\
 &= -i\hbar \frac{\int_{-\infty}^{\infty} \cos(kx) (-k \sin(kx)) dx}{\int_{-\infty}^{\infty} \cos^2(kx) dx} \\
 &= i\hbar k \frac{\int_{-\infty}^{\infty} \cos(kx) \sin(kx) dx}{\int_{-\infty}^{\infty} \cos^2(kx) dx}
 \end{aligned}$$

Notice that the integral in the numerator evaluates to zero (by symmetry) so that the average momentum of  $\psi_2(x)$  is  $\langle p_2 \rangle = 0$ . How are these results related, if at all? We can take the analysis one step further by recognizing that by Euler's formula, we can write  $\cos(kx) = \frac{1}{2}(e^{-ikx} + e^{ikx})$ . Therefore, the cosine function can be thought of as a superposition of waves defined by the wave functions  $\psi_+(x) = e^{ikx}$  and  $\psi_-(x) = e^{-ikx}$ . We've determined the average momentum of  $\psi_-(x)$  a moment ago as  $-k\hbar$  and the average momentum of  $\psi_+(x)$  can be readily determined as  $+k\hbar$ . So, for the wave function  $\cos(kx)$ , half of the time the momentum will be measured as  $-k\hbar$  and the other half of the time it will be measured as  $+k\hbar$ . Hence, the average momentum must come to zero, as illustrated.

## The Ehrenfest Theorem

### 11.2.5 Time Evolution of a Quantum Mechanical System

The fifth postulate of quantum mechanics we'll concern ourselves with can be stated as follows:

*The evolution in time of a quantum mechanical system is governed by the time-dependent Schrödinger equation,*

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t} \quad (11.2.11)$$

### 11.2.6 The Indistinguishability of Electrons

The sixth postulate of quantum mechanics we'll concern ourselves with can be stated as follows:

*Wave functions describing a many-electron system must be antisymmetric under the exchange of any two electrons.*

This postulate is more commonly referred to as the *Pauli exclusion principle*. Stated alternatively, the Pauli exclusion principle requires that the wave function for a multi-electron system be zero if all quantum numbers of any two electrons are the same.

## CHAPTER

# 12

# QUANTUM MECHANICAL MODELS OF TRANSLATIONAL MOTION

*One of the principal objects of theoretical research is to find the point of view from which the subject appears in the greatest simplicity*

- Josiah Willard Gibbs

We now venture to apply the Schrödinger equation and the postulates of quantum mechanics to some simple systems involving linear motion. We'll start by considering *the particle in a box* in one dimension and then in multiple dimensions. Importantly, we'll see that Bohr's assumptions regarding quantization of energy resulted from confinement of particles, such as electrons within an atom, and that multiple dimensions causes degeneracy among energy levels.

## 12.1 The Particle in a Box

*The particle in a box* is an example of a simple model that can be analyzed and discussed in great detail and has physical consequences which carry over to more complicated systems. Although a general solution to the wave function for a particle in a box will require some quantum mechanical postulates covered later, the model will stand as a good introduction to these postulates as well as the need for using mathematical intuition for solving problems in quantum mechanics.

We'll consider the case of some particle of mass  $m$  constrained to an interval on the  $x$ -axis defined by  $0 \leq x \leq L$  where  $L$  is some constant and is the size of the interval. Moreover, we'll start by considering a *free particle*, one in which there is no potential energy acting on the particle so that  $V(x) = 0$  in the Hamiltonian operator. Then, the Schrödinger equation can be rewritten as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x), \quad 0 \leq x \leq L$$

for some wave function  $\psi(x)$  where the ordinary differential (as opposed to partial differential) is considered

because we're in one dimension. Following a little bit of algebraic gymnastics we arrive at

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad (12.1.1)$$

which is a second-order, linear ordinary differential equation, a solution of which is provided in Appendix ???. Going through the motions, we find that a general solution to Equation (12.1.1) is given by

$$\psi(x) = c_1 e^{\frac{i\sqrt{2mE}}{\hbar}x} + c_2 e^{-\frac{i\sqrt{2mE}}{\hbar}x} \quad (12.1.2)$$

Using Euler's formula,  $e^{ix} = \cos x + i \sin x$ , we can rewrite the equation above as

$$\psi(x) = c_1 \cos\left(\frac{\sqrt{2mE}}{\hbar}x\right) + c_2 \sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) \quad (12.1.3)$$

which is what we commonly think of as representing some sort of wave. Many textbooks and references jump right to asserting that an equation of the form of (12.1.3) solves the wave equation. Now, you can (sorta) see where it comes from<sup>1</sup>.

At this point we can introduce boundary conditions to our particle. As described in the beginning we require the particle to be restricted on some interval  $0 \leq x \leq L$  so that  $\psi(0) = \psi(L) = 0$  and  $\psi(x) = 0$  for any  $x$  outside of the described interval. Using these conditions in Equation (12.1.3),

$$\psi(0) = c_1 \cos(0) + c_2 \sin(0) = c_1$$

implies that  $c_1 = 0$ . Invoking the second condition and adopting  $c_1 = 0$ ,

$$\psi(L) = c_2 \sin\left(\frac{\sqrt{2mE}}{\hbar}L\right) = 0$$

This implies that  $L\sqrt{2mE}/\hbar = n\pi$  for any integer  $n = 1, 2, 3, \dots$ . *This is an important result*, for more than one reason. As a brief aside, notice that we can rewrite the relation as

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}, \quad n = 1, 2, 3, \dots \quad (12.1.4)$$

*which are the quantized energy levels of the particle in a box.* These are the only physically meaningful solutions to the Schrödinger equation. Notice that quantization arises naturally from the boundary conditions, in contrast to how they were introduced by Planck and Bohr in a manner that was just sorta guessing. In a series of papers introducing the laws of quantum mechanics, Schrödinger introduced this relationship as follows:

I wish to show that the usual rules of quantization can be replaced by another postulate (the Schrödinger equation) in which there occurs no mention of whole numbers. Instead, the introduction of integers arises in the same natural way as, for example, in a vibrating string, for which the number of nodes is integral. The new conception can be generalized, and I believe that it penetrates deeply into the true nature of quantum rules.

Before moving on we can relate our intuition about the connection between classical and quantum mechanics to this result. In Equation (12.1.4), notice that the energy gaps decrease as either  $L$  increases or as  $m$  increases. That is, the gap between allowed energies decreases as size of the box increases or as the mass of the particle increases. The latter of these two results agrees with what we already know about classical mechanics: the energy spectrum is continuous! The former of these two results provides another reason for quantization as a result of confinement. If the particle was not at all confined, that is,  $L$  grows very large, the gap in the

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<sup>1</sup>Like I hinted at briefly, refer to the Appendix for more discussion on solving second-order differential equations.

allowed energies decreases<sup>2</sup>.

If that wasn't enough there's also another amazing result we can draw from this. Recall the de Broglie relation,  $\lambda = h/p$ , for the momentum  $p$  of some particle. Also, notice that for a free particle (i.e., the one we've been considering this whole time) the momentum is given by  $p = \sqrt{2mE}$ . Making this substitution into the relation  $L\sqrt{2mE}/\hbar = n\pi$ ,

$$\begin{aligned} n\pi &= \frac{Lh}{\lambda\hbar} \\ &= \frac{2L\pi}{\lambda} \\ \lambda &= \frac{2L}{n} \end{aligned} \tag{12.1.5}$$

which are the normal modes of the wave function for a particle in a box. The wonderful part about solving Schrödinger's equation for this particle without making any large assumptions is that the derivation for a result like Equation (12.1.5) becomes clear.

With the brief aside concluded, we can return to finding the wave function for the particle in a box. Using the relationship  $L\sqrt{2mE}/\hbar = n\pi$  and  $c_1 = 0$  as we've already shown,

$$\psi(x) = c_2 \sin\left(\frac{n\pi x}{L}\right) \tag{12.1.6}$$

is our current result. To determine the constant  $c_2$  we'll use the fact that all wave functions must be properly normalized. That is,

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

where  $\psi^*(x)$  represents the wave function's complex conjugate. This postulate, sometimes referred to as *the Born rule*, will be discussed in greater detail later. For now, though, we'll just utilize the result. We can start by trying to normalize Equation (12.1.6). Note that since the wave function does not have a complex component,  $\psi^*(x) = \psi(x)$ .

$$\begin{aligned} \int_{-\infty}^{\infty} c_2 \sin\left(\frac{n\pi x}{L}\right) c_2 \sin\left(\frac{n\pi x}{L}\right) dx &= c_2^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx \\ &= c_2^2 \int_0^L \left(\frac{1}{2} - \cos\left(\frac{2n\pi x}{L}\right)\right) dx \\ &= c_2^2 \left[ \frac{1}{2}x - \frac{L}{2n\pi} \sin\left(\frac{2n\pi x}{L}\right) \right]_0^L \\ &= c_2^2 \left(\frac{L}{2}\right) \end{aligned}$$

In order for this integral to evaluate to 1, we require  $c_2 = \sqrt{2/L}$  and so our normalized wave function for a particle in a box becomes

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad 0 \leq x \leq L, \quad n = 1, 2, 3, \dots \tag{12.1.7}$$

If we instead had begun our analysis by asserting that the wave function must look something like a trig function, and gone through the motions to arrive at Equation (12.1.7), we could also attain the energy of the wave function for each mode using the Schrödinger equation, operating on  $\psi(x)$  via the Hamiltonian operator.

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<sup>2</sup>If we allow  $L \rightarrow \infty$  we find that  $E \rightarrow 0$  in Equation (12.1.4). Clearly, this is untrue because quantum particles cannot have zero energy. This is because the formula for the energy we derived here is for a particle confined to a box and the energy for an unconfined particle is different. Though, it does provide some evidence for quantization being a product of confinement, regardless.

Recall that in this case we are considering a free particle so that  $V(x) = 0$  while  $0 \leq x \leq L$ .

$$\begin{aligned}
 \hat{H}\psi(x) &= \left\{ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right\} \left[ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right] \\
 &= -\frac{\hbar^2}{2m} \sqrt{\frac{2}{L}} \frac{\partial^2}{\partial x^2} \left[ \frac{n\pi}{L} \cos\left(\frac{n\pi x}{L}\right) \right] \\
 &= -\frac{\hbar^2}{2m} \sqrt{\frac{2}{L}} \left( -\frac{n^2\pi^2}{L^2} \sin\left(\frac{n\pi x}{L}\right) \right) \\
 &= \frac{\hbar^2 n^2 \pi^2}{2mL^2} \psi(x) \\
 &= E\psi(x)
 \end{aligned}$$

and therefore  $E = \hbar^2 n^2 / 8mL^2$  as expected. This method of determining some physically relevant parameter using an operator can be done using any other operator as well, such as the position or momentum operators.

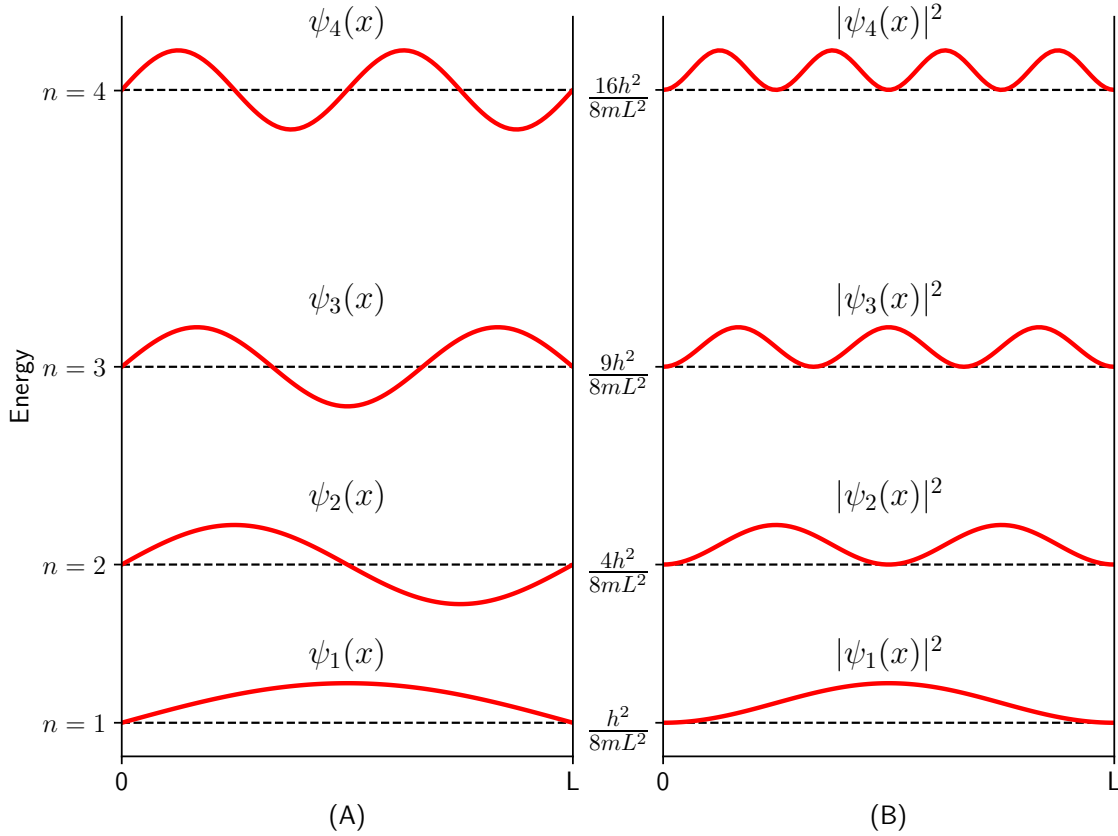


Figure 12.1: (A) The wave function of the first four energy levels of a particle in a box, with the corresponding probability densities in (B).

Figure 12.1 illustrates the plots of the Equation (12.1.7) for the  $n = 1, 2, 3$  and 4 energy levels and the associated probability distributions. The horizontal dotted lines are the energy levels, given by Equation (12.1.4). It is important to know how many states exist having the energy corresponding to a given level. For example, how many states exist having the energy  $E_3$ ? For  $n = 3$ , there is only one wave function,  $\psi_3(x)$ , which leads to this energy level. For the particle in a box, this is true for every energy level. Stated more fancily, we say that each energy level is *nondegenerate*.

*Degeneracy* is an important topic as it relates energy levels of a system to one another as well as the wave

function of the system. As noted above, a nondegenerate energy level is one that can only be represented by a single wave function (you might also say that the energy level is *singly degenerate* or has a *degeneracy* of 1). In contrast, if two or more eigenfunctions of a quantum mechanical system give the same value for some observable of the system, say, energy, then the states are said to be *degenerate*. Mathematically, this is represented by the Hamiltonian (keeping with the theme of energy) for the system having more than one linearly independent eigenfunction with the same eigenvalue.

### 12.1.1 Zero Point Energy

As is illustrated in Figure 12.1 and as was probably mentioned by me sometime earlier, the lowest energy state for a particle in a box is the  $n = 1$  level, corresponding to an energy of  $E_1 \approx 0.38 \text{ eV}$ . Unlike a classical particle which may have a stationary state corresponding to  $E = 0$ , *a quantum mechanical particle in a box cannot be at rest*. This would violate the uncertainty principle. Stated more technically, *a confined particle cannot be at rest*.

Although the particle's position and velocity are uncertain, the particle's energy in each state can be precisely determined. The distinction between an uncertain position and velocity is strange, however, it is a natural consequence of a standing wave. In order to *have* a standing state at all, a particle must form a standing wave which only occurs for very precise frequencies and thus precise energies.

### 12.1.2 Wave Function Symmetry and Orthogonality

Figure 12.1 illustrates the powerful result that  $\psi^2(x)$  is symmetric about the center of the box. That is, the particle is equally likely to be found in either half of the box. This agrees with our intuition; there's no reason for the particle to favor one side of the box over another. By the rules of symmetry (refer to Appendix ??) then, we know that  $\psi$  must be either a symmetric or antisymmetric function. Also in Figure 12.1 are the wave functions for each energy level; clearly,  $\psi_1$  and  $\psi_3$  are symmetric about the center of the box while  $\psi_2$  and  $\psi_4$  are antisymmetric.

These observations (along with a proof that I don't care for) justify the following result: *A nondegenerate eigenfunction must be symmetric or antisymmetric under any invariant operator*. By "invariant operator" we mean one which does not change with some transformation of the system. An example of this would be the Hamiltonian operator under a transformation of coordinates; although the positions and momenta of each particle would change in this case, the total energy and therefore total energy operator would remain unchanged. Hence,  $\hat{H}$  is considered invariant under a coordinate transformation.

Knowing stuff about the eigenfunctions of a system is great, especially when the wave functions are considered on their own. We've already seen how the product of an eigenfunction and itself has a probabilistic interpretation. This motivates us to consider an interpretation for the product of two wave functions which represent different energy levels. That is, what does

$$\int_{-\infty}^{\infty} \psi_m(x) \psi_n(x) dx$$

mean? Conveniently, the requirement that all quantum mechanical operators must be Hermitian imposes another restriction on the eigenfunctions of quantum mechanical operators such that this integral may be evaluated with ease.

Consider the two eigenvalue equations,

$$\hat{A}\psi_n = a_n\psi_n \quad \& \quad \hat{A}\psi_m = a_m\psi_m$$

where  $\hat{A}$  represents any of the quantum mechanical operators we are familiar with and  $\psi_i$  is some eigenfunction for the system with a corresponding eigenvalue  $a_i$ . Since  $\psi_m$  and  $\psi_n$  are eigenfunctions of the system, we

have that

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A} \psi_n dx = \int_{-\infty}^{\infty} \psi_m^* a_n \psi_n dx = a_n \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \quad (12.1.8)$$

similar to result of postulate 4. Since  $\hat{A}$  is a Hermitian operator we can also write

$$\int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx = \left[ \int_{-\infty}^{\infty} \psi_n^* \hat{A} \psi_m dx \right]^* = \left[ \int_{-\infty}^{\infty} \psi_n^* a_m \psi_m dx \right]^* = a_m^* \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \quad (12.1.9)$$

by Equation (11.2.6) for the definition of a Hermitian operator. Subtracting Equations (12.1.8) and (12.1.9) affords

$$\int_{-\infty}^{\infty} \psi_m^* \hat{A} \psi_n dx - \int_{-\infty}^{\infty} \psi_n \hat{A}^* \psi_m^* dx = (a_n - a_m^*) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad (12.1.10)$$

with equality to zero at the end by the definition of a Hermitian matrix, given in Equation (11.2.7).

At this point we have two possibilities to consider, either  $n = m$  or  $n \neq m$ . If  $n = m$ , the integral in Equation (12.1.10) must evaluate to 1 by normalization and therefore  $a_n = a_m^*$ . This is simply a proof that the eigenvalues of a Hermitian transformation are real! If  $n \neq m$ , it must be the case that

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0, \quad n \neq m \quad (12.1.11)$$

Thus, we've proved that the eigenfunctions for a Hermitian operator are orthogonal for a nondegenerate system. For the particle in a box, this guarantees that any integral of the form in Equation (12.1.11) with  $n \neq m$  goes to zero and therefore all energy states are nondegenerate. Conversely, since all of our solutions to the eigenfunctions for a particle in a box are nondegenerate, they form an orthogonal set. Moreover, since we've properly normalized all wave functions in this set, they form an *orthonormal set*.

To get an idea of how this helps us determine properties of some physical systems we'll run through an example. Suppose we have a particle in a box that can be described similarly to how we've done so far, with mass  $m$  in a box of length  $L$ . The wave function for this particle is given by

$$\psi(x, t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad 0 < x < L$$

Suppose that at time  $t = 0$  the particle can be described by a superposition of wave functions with each in a different energy state,

$$\psi(x, 0) = \frac{1}{2}\phi_1(x) + \frac{\sqrt{3}}{2}\phi_3(x) \quad (12.1.12)$$

where  $\phi_j(x)$  is the wave function for a particle in the  $n = j$  energy level. If we sample  $10^6$  identically prepared systems with the same wave functions (described above), what is the average value of the energy measured? To determine the average energy we'll first make some observations about how coefficients of  $\phi_1$  and  $\phi_3$ . Suppose that we did not know the coefficients in Equation (12.1.12) and tried to determine the total energy of the system:

$$\hat{H}\psi = \hat{H}(c_1\phi_1 + c_3\phi_3) = c_1\hat{H}\phi_1 + c_3\hat{H}\phi_3 = c_1E_1\phi_1 + c_3E_3\phi_3 = E\psi$$

Here,  $c_1$  and  $c_3$  are taking the place of  $1/2$  and  $\sqrt{3}/2$  for the time being. Now, we see that the total energy of the system must be  $E = c_1E_1 + c_3E_3$ . Continuing to suspend reality and pretending that we did not know  $c_1$  and  $c_3$ , we could determine them by using the postulates of quantum mechanics. Since  $|\psi(x)|^2$  defines a

probability distribution,

$$\begin{aligned}
\int_{-\infty}^{\infty} |\psi(x)|^2 dx &= \int_{-\infty}^{\infty} (c_1\phi_1 + c_3\phi_3)^2 dx \\
1 &= \int_{-\infty}^{\infty} c_1^2\phi_1^2 + 2c_1c_3\phi_1\phi_3 + c_3^2\phi_3^2 dx \\
&= \int_{-\infty}^{\infty} c_1^2\phi_1^2 + c_3^2\phi_3^2 dx \\
&= c_1^2 \int_{-\infty}^{\infty} \phi_1^2 dx + c_3^2 \int_{-\infty}^{\infty} \phi_3^2 dx \\
1 &= c_1^2 + c_3^2
\end{aligned} \tag{12.1.13}$$

In the second and final lines we took advantage of the fact that all of the wave functions are normalized so that integrating their squares evaluates to one. In the third line we took advantage of the orthogonality of eigenfunctions. Thus, we see that the coefficients of the eigenfunctions in a superposition must be normalized. More generally, we could say that for a wave function composed of  $n$  eigenfunctions,

$$\psi(x) = \sum_{i=1}^n c_i \phi_i(x), \quad 1 = \sum_{i=1}^n c_i^2 \tag{12.1.14}$$

Awesome! That didn't answer our question about energy though. Recall that the average value of an observable is given by

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) dx$$

for a normalized wave function  $\psi(x)$  and operator  $\hat{A}$  with corresponding observable  $a$ . Using the Hamiltonian and substituting Equation (12.1.12) maintaining the use of  $c_1$  and  $c_2$ , we have that the average energy of a system is

$$\begin{aligned}
\langle E \rangle &= \int_{-\infty}^{\infty} (c_1\phi_1 + c_3\phi_3) \hat{H} (c_1\phi_1 + c_3\phi_3) dx = \int_{-\infty}^{\infty} (c_1\phi_1 + c_3\phi_3) (c_1\hat{H}\phi_1 + c_3\hat{H}\phi_3) dx \\
&= \int_{-\infty}^{\infty} (c_1\phi_1 + c_3\phi_3) (c_1E_1\phi_1 + c_3E_3\phi_3) dx \\
&= \int_{-\infty}^{\infty} (c_1^2E_1\phi_1^2 + 2c_1c_3E_1E_3\phi_1\phi_3 + c_3^2E_3\phi_3^2) dx \\
&= \int_{-\infty}^{\infty} c_1^2E_1\phi_1^2 dx + \int_{-\infty}^{\infty} c_3^2E_3\phi_3^2 dx \\
\langle E \rangle &= c_1^2E_1 + c_3^2E_3
\end{aligned} \tag{12.1.15}$$

Thus, we find that the average energy is *not* simply a linear combination of the energies using the coefficients of the wave functions; by the postulate of quantum mechanics regarding average values, we see that we gotta square those coefficients to get the total energy. Notice that at no point in finding Equation (12.1.15) did we make any moves specific to the Hamiltonian operator. So, we could generalize this result to any operator:

$$\langle a \rangle = \sum_{i=1}^n c_i^2 a_i \tag{12.1.16}$$

Above,  $a$  is some observable and  $c_i$  is the coefficient of an eigenfunction of the wave function, as described earlier. Finally, we can derive the average energy of the system initially described. Recall that the energy of a particle in a box with a wave function of principle quantum number  $n$  is given by  $E_n = h^2 n^2 / 8mL^2$ . So, the



total energy of our wave function is at time  $t = 0$  is

$$\begin{aligned}\langle E \rangle &= \left(\frac{1}{2}\right)^2 E_1 + \left(\frac{\sqrt{3}}{2}\right)^2 E_3 \\ &= \frac{1}{4} \left(\frac{h^2(1)^2}{8mL^2}\right) + \frac{3}{4} \left(\frac{h^2(3)^2}{8mL^2}\right) \\ &= \frac{7h^2}{8mL^2}\end{aligned}$$

Lastly, suppose that we ran this exact experiment a second time, this time 20 minutes later at  $t = 1200$ . What is the average value of the energy at that point? Clearly, the it will be the same since energy is a conserved quantity.

### 12.1.3 The Particle Outside of a Box

The particle outside of a box is just another way of saying an unconfined particle. We can start the same we did in dealing with a particle in a box, assuming that the particle has some mass  $m$  and that it's a free particle so that it experiences no potential energy. The Schrödinger equation becomes

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = E\psi(x)$$

for a wave function  $\psi(x)$  which describes the particle. Earlier in Section 12.1 we saw that the general solution to this equation was

$$\psi(x) = c_1 e^{\frac{i\sqrt{2mE}}{\hbar}x} + c_2 e^{-\frac{i\sqrt{2mE}}{\hbar}x}$$

Unlike in the case of a particle confined to a box, however, there are no boundary conditions on a particle outside of a box. Hence, there are no restrictions on the allowed values of the energy and therefore the energy is not quantized. Hence, *quantization is a result of confinement*. I think I mentioned that earlier but it's important so thought I'd reiterate it.

### 12.1.4 Pi Electrons in a Conjugated System

Absorption of light in the visible or ultraviolet portion of the electromagnetic spectrum results in electron excitation from lower-energy occupied orbitals to higher-energy unoccupied orbitals. The subsequent relaxation of electrons back into their lower lying states causes light emission. Conjugated systems allow for electron delocalization; the greater the degree of delocalization the more the absorption maximum is red-shifted (that is, the frequency required for absorption is decreased). The energy levels for such linearly conjugated systems is described quite well by the particle in a box model.

Suppose we consider the series of linearly conjugated systems involving butadiene, hexatriene, and octatetraene, that is, the alkenes with two, three, and four  $\pi$  bonds, respectively. The wavelength of maximum absorption,  $\lambda_{\max}$ , for each of these is 217 nm, 268 nm, and 304 nm, respectively. All of these quantities can be computed experimentally using a UV/Vis spectrometer. Using these values, how can we estimate the length of any one of these molecules?

We'll do this by modeling the electrons within the conjugated systems as particles in a box and assume that they won't leave the system so that the box has infinitely high walls. The energy levels for this sort of system has been determined already and is given by  $E_n = h^2 n^2 / 8mL^2$  for some principle quantum number  $n$  and box length  $L$ . Also, we've found that the difference between two energy levels can be written as  $\Delta E_{n_1 \rightarrow n_2} = \frac{h^2}{8mL^2} (n_2^2 - n_1^2)$ . In this instance we're interested in trying to find the length of the "box" so that

we'll rewrite this expression as

$$L = \sqrt{\frac{h^2(n_2^2 - n_1^2)}{8m\Delta E}}, \quad n_2 > n_1 \quad (12.1.17)$$

where the particle is excited from the  $n_1$  to the  $n_2$  level. With the wavelengths of maximum absorption we can compute the change in energy between energy levels for each system Planck's relation,  $\Delta E = hc/\lambda_{\max}$ . So, all that's left is to determine the ground state energy levels and first excited state levels. For butadiene, with two  $\pi$  bonds there are four  $\pi$  electrons. Since two electrons occupy each energy level (the Pauli Exclusion Principle) the lowest lying energy level is  $n = 2$ . Similar arguments can be made for hexatriene and octatetraene which have lowest lying energy levels of  $n = 3$  and  $n = 4$ , respectively. The first excited state energy levels for all of these is simply  $n + 1$ . Using butadiene as an example, the length of the conjugated system can be estimated as

$$\begin{aligned} L_{\text{C}_4\text{H}_6} &= \sqrt{\frac{h^2(n_2^2 - n_1^2)}{8m(hc/\lambda_{\max})}} = \sqrt{\frac{h(n_2^2 - n_1^2)\lambda_{\max}}{8mc}} \\ &= \sqrt{\frac{(6.626 \times 10^{-34} \text{ J s})(3^2 - 2^2)(217 \text{ nm})}{8(9.109 \times 10^{-31} \text{ kg})(2.998 \times 10^8 \text{ m/s})}} \\ &= 5.736 \text{ \AA} \end{aligned}$$

The calculated lengths of butadiene, hexatriene, and octatetraene are reported in Table 12.1. Although rough, the particle in a box model provides a fair estimate for the length of the conjugated molecule. Most importantly, this model correctly predicts that the length of the chain will increase as conjugation increases.

Alkene	Estimated Length (Å)	Calculated Length (Å)
Butadiene	5.736	4.130
Hexatriene	7.543	6.922
Octatetraene	9.109	9.714

Table 12.1: Estimated molecule lengths using particle in a box model versus calculated lengths from the literature. C=C and C-C bond lengths taken from Craig, et. al.

## 12.2 The Particle in a 3-Dimensional Box

The particle in a three-dimensional box is conceptually similar to the particle in a one-dimensional box. The only difference is in the number of dimensions we have to consider. Recall that the three-dimensional Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x, y, z) + V(x, y, z)\psi(x, y, z) = E\psi(x, y, z)$$

where  $\nabla^2$  is the Laplacian operator. If we suppose that some particle of mass  $m$  is confined to a box of defined on the intervals  $0 < x < a$ ,  $0 < y < b$ , and  $0 < z < c$  where the potential energy inside the box is  $V(x, y, z) = 0$ , the Schrödinger equation can be rewritten as

$$\begin{aligned} &-\frac{\hbar^2}{2m}\nabla^2\psi(x, y, z) = E\psi(x, y, z) \\ &-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x, y, z) = E\psi(x, y, z), \quad 0 < x < a, 0 < y < b, 0 < z < c \end{aligned} \quad (12.2.1)$$

Notice that we can separate the total energy operator into three components, each representing the energy in that respective direction. That is, Equation (12.2.1) can be rewritten as

$$(\hat{H}_x + \hat{H}_y + \hat{H}_z) \psi(x, y, z) = E \psi(x, y, z) \quad (12.2.2)$$

Whenever this sort of separation of variables is possible, we can rewrite the wave function  $\psi(x, y, z)$  as a product of wave functions in each direction. So, we can write  $\psi(x, y, z) = \mathcal{X}(x)\mathcal{Y}(y)\mathcal{Z}(z)$  where  $\mathcal{X}(x)$ ,  $\mathcal{Y}(y)$ , and  $\mathcal{Z}(z)$  are the wave functions in the  $x$ -,  $y$ -, and  $z$ -directions, respectively. Now, after some algebraic gymnastics, we can rewrite Equation (12.2.2) as

$$\begin{aligned} (\hat{H}_x + \hat{H}_y + \hat{H}_z) \psi(x, y, z) &= E \psi(x, y, z) \\ (\hat{H}_x + \hat{H}_y + \hat{H}_z) \mathcal{X}(x)\mathcal{Y}(y)\mathcal{Z}(z) &= E \mathcal{X}(x)\mathcal{Y}(y)\mathcal{Z}(z) \\ \mathcal{Y}\mathcal{Z}\hat{H}_x\mathcal{X} + \mathcal{X}\mathcal{Z}\hat{H}_y\mathcal{Y} + \mathcal{X}\mathcal{Y}\hat{H}_z\mathcal{Z} &= \\ \frac{\hat{H}_x\mathcal{X}}{\mathcal{X}} + \frac{\hat{H}_y\mathcal{Y}}{\mathcal{Y}} + \frac{\hat{H}_z\mathcal{Z}}{\mathcal{Z}} &= E \end{aligned} \quad (12.2.3)$$

In the second to last step we divided the expression through by  $\mathcal{X}\mathcal{Y}\mathcal{Z}$ . Equation (12.2.3) illustrates the fact that we can solve the three-dimensional particle in a box problem by solving three one-dimensional particle in a box problems instead. If we consider some change in the system in the  $x$ -direction, clearly the  $y$  and  $z$  components of the wave function ( $\mathcal{Y}(y)$  and  $\mathcal{Z}(z)$ , respectively) do not change and so we're left with

$$\frac{\hat{H}_x\mathcal{X}}{\mathcal{X}} + (\text{constant}) + (\text{constant}) = E$$

which shows us that even though the variable  $x$  is changing, the expression  $\hat{H}_x\mathcal{X}/\mathcal{X}$  does not change since the total energy of the system  $E$  is constant by the conservation of energy. Let's say that the energy contribution from the  $x$  component of the wave function is some constant  $E_x$  so that  $\hat{H}_x\mathcal{X}/\mathcal{X} = E_x$ . We can make analogous arguments for the  $y$  and  $z$  components of the wave function so that we're left with a system of three equations,

$$\frac{\hat{H}_x\mathcal{X}}{\mathcal{X}} = E_x, \quad \frac{\hat{H}_y\mathcal{Y}}{\mathcal{Y}} = E_y, \quad \frac{\hat{H}_z\mathcal{Z}}{\mathcal{Z}} = E_z \quad (12.2.4)$$

where the total energy  $E = E_x + E_y + E_z$  of the system is the sum of the energy contributions from each direction. Considering any one of the three expressions in Equation (12.2.4) (I chose the  $x$  component) reveals the eigenvalue equation  $\hat{H}_x\mathcal{X} = E_x\mathcal{X}$  which is exactly the one-dimensional particle in a box problem. Recalling our solution to this problem from Equation (12.1.7) as well as the energy associated with the particle in a box from Equation (12.1.4), the  $x$ ,  $y$ , and  $z$  components of the three-dimensional particle in a box are solved by

$$\begin{aligned} \mathcal{X}(x) &= \sqrt{\frac{2}{a}} \sin\left(\frac{n_x\pi x}{a}\right), & E_{n_x} &= \frac{h^2 n_x^2}{8ma^2}, & 0 < x < a \\ \mathcal{Y}(y) &= \sqrt{\frac{2}{b}} \sin\left(\frac{n_y\pi y}{b}\right), & E_{n_y} &= \frac{h^2 n_y^2}{8mb^2}, & 0 < y < b \\ \mathcal{Z}(z) &= \sqrt{\frac{2}{c}} \sin\left(\frac{n_z\pi z}{c}\right), & E_{n_z} &= \frac{h^2 n_z^2}{8mc^2}, & 0 < z < c \end{aligned}$$

Recall that we began by asserting separability in the wave function so that  $\psi(x, y, z) = \mathcal{X}(x)\mathcal{Y}(y)\mathcal{Z}(z)$ . Also, we defined the total energy to be a sum of the directional energies,  $E = E_x + E_y + E_z$ . Thus, the wave function

of a three-dimensional particle in a box and the associated energy is given by

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right), \quad 0 < x < a, \quad 0 < y < b, \quad 0 < z < c \quad (12.2.5)$$

$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right), \quad n_x, n_y, n_z \in \{1, 2, 3 \dots\} \quad (12.2.6)$$

Figure ?? illustrates the wave functions for the three-dimensional particle in a box for different combinations of quantum numbers  $n_x$ ,  $n_y$ , and  $n_z$ .

### 12.2.1 The Particle in a Cube

A cubical version of the particle in a box is useful for a further understanding of behavior of energy levels in the particle in a box. Here, we'll consider boxes where the lengths of the intervals in each of the  $x$ ,  $y$ , and  $z$  directions is the same so that  $a = b = c = L$ , using the definitions for  $a$ ,  $b$ , and  $c$  as in the previous section. Then, our solution to the wave function for the three-dimensional particle in a box becomes

$$\psi(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

$$E_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

The lowest allowed energy levels for any of  $n_x$  and  $n_y$  or  $n_z$  is 1 so that the lowest allowed energy (the zero-point energy) of the wave function is  $E_{1,1,1} = 3h^2/8mL^2$ . The next lowest energy comes from allowing any one of  $n_x$ ,  $n_y$ , or  $n_z$  to be 2, corresponding to an energy of  $E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = 6h^2/8mL^2$ . Notice that allowing  $n_x = 2$  and  $n_y = n_z = 1$  produces a different wave function than allowing  $n_y = 2$  and  $n_x = n_z = 1$  yet both combinations produce the same energy. Thus, the second energy levels for a three dimensional particle in a box is *triply degenerate* because three independent eigenfunctions produces the same energy.

## 12.3 The Particle in a Finite Depth Box

The particle in a box model can be used to explore concepts such as why core electrons are not involved in chemical bonds, the stabilizing effect of delocalized  $\pi$  electrons in aromatic molecules, and the ability of metals to conduct electrons. Before applying the model to more “real world” scenarios, though, it must be modified to be made more realistic. This is done by letting the box have a finite depth, allowing particles to escape similar to how we might think of ionization or delocalization.

Suppose that we take the model of a particle in a box that we've been considering so far for a box of width  $L$ . For  $-L/2 < x < L/2$ , the potential energy of the system is  $V(x) = 0$ . For  $x < -L/2$  and  $L/2 < x$ , instead of allowing  $V(x) = \infty$  we instead adopt the convention  $V(x) = V_0$  so that if the particle has *enough* energy it may escape the box. We can divide the system into three regions, each with their own wave function  $\psi(x)$ ,

$$\text{Region 1} \quad V(x) = V_0 \quad \text{for } x < -L/2$$

$$\text{Region 2} \quad V(x) = 0 \quad \text{for } -L/2 < x < L/2$$

$$\text{Region 3} \quad V(x) = V_0 \quad \text{for } L/2 < x$$

where the center of the box is located equidistant from each end. As before, in region 2 where  $V(x) = 0$  we have that the wave function must be  $\psi_2(x) = A \sin(n\pi x/L)$  for some amplitude  $A$ . Notice that we can rewrite the scaling term inside the sine function using the relationship  $E_n = h^2 n^2 / 8mL^2$  for the energies of a particle in a

box, the de Broglie relation, and the momentum of a particle in a region of zero potential energy,  $p = \sqrt{2mE}$ :

$$\frac{n\pi x}{L} = \pi x \left( \sqrt{\frac{8mE_n}{h^2}} \right) = \pi x \left( \frac{2\sqrt{2mE_n}}{h} \right) = \pi x \left( \frac{2p}{h} \right) = \frac{2\pi x}{\lambda} \quad (12.3.1)$$

Now, the wave function for the particle in a box in a region of zero potential can be written as  $\psi_2(x) = A \sin(2\pi x/\lambda)$ . In regions of potential  $V = V_0$  the total kinetic energy of the particle is expressed as  $T = E - V_0$  and therefore the wavelength of the particle will be greater than if the potential were zero, since energy is inversely proportional to wavelength. This implies that we require a longer-wavelength sinusoid for  $x < -L/2$  and  $L/2 < x$  be *smoothly* connected to a shorter-wavelength sinusoid for  $-L/2 < x < L/2$ . In other words, the wave functions in all regions must be continuous and differentiable at the boundaries  $x = \pm L/2$ . Although the wavelengths are determined by the difference in energy  $E - V_0$ , the amplitude of the waves outside of the “box” is free to change. This degree of freedom is *always* enough to allow a smooth joining of waves. Moreover, since a particle can possess any energy greater than the potential outside of the box  $V_0$ , when it escapes the box its energies are no longer quantized. Such unquantized states are referred to as *continuum states*.

Of brief note is the coefficient on  $x$ ,  $2\pi/\lambda$ . Notice that we may define a new constant with a relationship to the energy of the system as

$$\eta = \frac{\lambda}{2\pi} = \frac{h}{2\pi p} = \frac{\hbar}{\sqrt{2m(V_0 - E)}} \quad (12.3.2)$$

It may be shown that  $\eta$  has units of meters and is referred to as the *penetration distance*. Interestingly, this relation reveals that even for incredibly small energies  $E$ , particles penetrate into the classically forbidden region. Because of wave-particle duality, an atomic particle is “fuzzy” with no well-defined edge. Moreover, the penetration distance increases as  $E$  is allowed to increase.

Now we turn our attention to regions of nonzero potential energy. We can apply de Broglie’s relationship  $\lambda = h/p = h/\sqrt{2m(E - V_0)}$  to express the wavelength of the particle at any point in space as a function of its energy, since  $V_0$  is constant. Assuming that the particle remains in the box and its total energy is less than that capable of escaping the box,  $E < V_0$  and *the wavelengths are imaginary*. Another consequence of this is that the kinetic energy is less than zero and therefore *the momentum of the particle is imaginary* too. This region is referred to as the *classically forbidden region*.

Recall that in Equation (12.1.2) we expressed solutions to the particle in a box with imaginary exponentials through Euler’s formula. Here we’ll take a similar approach to write solutions to the wave function of a particle in regions of nonzero potential as

$$\psi_1(x) = Ae^{\frac{2\pi i}{\lambda_1}x} + Be^{-\frac{2\pi i}{\lambda_1}x}, \quad \psi_3(x) = Fe^{\frac{2\pi i}{\lambda_3}x} + Ge^{-\frac{2\pi i}{\lambda_3}x}$$

where  $\psi_1(x)$  and  $\psi_3(x)$  represent wave functions in regions 1 and 3, respectively, and  $A$ ,  $B$ ,  $F$ , and  $G$  are some constants dependent on the energy of the system. In region 1 where  $x < -L/2$ , in order for  $\psi_1^*(x)\psi_1(x)$  to be integrable as  $x \rightarrow -\infty$  it must be the case that  $B = 0$ . Similarly for  $\psi_3(x)$  where  $x > L/2$  we require  $F = 0$  in order to evaluate the behavior of the wave function as  $x \rightarrow \infty$ . So, the wave functions in all regions may be expressed as

$$\psi_1(x) = Ae^{\frac{2\pi i}{\lambda_1}x}, \quad \psi_2(x) = C \sin\left(\frac{2\pi x}{\lambda_2}\right), \quad \psi_3(x) = Ge^{-\frac{2\pi i}{\lambda_3}x}$$

Now we must join the expression at the boundaries  $x = \pm L/2$ , that is, determine the value of the coefficients which make the wave functions at the border of each region smooth and continuous. By symmetry, the process of determining the coefficients will be the same whether we consider the boundary between regions 1 and 2 or 2 and 3. I’ll proceed with the analysis by considering the boundary of regions 2 and 3. We require

that

$$C \sin\left(\frac{2\pi(L/2)}{\lambda_2}\right) = Ge^{-\frac{2\pi i}{\lambda_3}(L/2)} \quad (12.3.3)$$

by continuity. We also require that

$$\frac{\partial}{\partial x} \left[ C \sin\left(\frac{2\pi x}{\lambda_2}\right) \right] = \frac{\partial}{\partial x} \left[ Ge^{-\frac{2\pi i}{\lambda_3}x} \right] \Rightarrow \frac{2\pi C}{\lambda_2} \cos\left(\frac{2\pi x}{\lambda_2}\right) = -\frac{2\pi i G}{\lambda_3} e^{-\frac{2\pi i}{\lambda_3}x} \quad (12.3.4)$$

in order for the wave functions to form a smooth function. We can substitute our expression from Equation (12.3.3) into (12.3.4) to obtain

$$\frac{2\pi C}{\lambda_2} \cos\left(\frac{2\pi(L/2)}{\lambda_2}\right) = -\frac{2\pi i C}{\lambda_3} \sin\left(\frac{2\pi(L/2)}{\lambda_2}\right)$$

which affords the condition

$$\tan\left(\frac{2\pi(L/2)}{\lambda_2}\right) = \frac{i\lambda_3}{\lambda_2}$$

Finally, using the de Broglie relation for  $\lambda_2 = h/\sqrt{2mE}$  and  $\lambda_3 = h/\sqrt{2m(E - V_0)}$  we see that

$$\begin{aligned} \tan\left(\frac{2\pi(L/2)}{h/\sqrt{2mE}}\right) &= \frac{ih/\sqrt{2m(E - V_0)}}{h/\sqrt{2mE}} \\ &= \frac{i\sqrt{E}}{\sqrt{E - V_0}} \\ &= \frac{i^2\sqrt{E}}{\sqrt{V_0 - E}} \\ \tan\left(\frac{2\pi(L/2)\sqrt{2mE}}{h}\right) &= -\frac{\sqrt{E}}{\sqrt{V_0 - E}} \end{aligned} \quad (12.3.5)$$

where the only unknown is the total energy  $E$ . In the second to last line I took advantage of the fact that from the beginning we assumed that  $E < V_0$  which allowed us to get rid of the imaginary unit  $i$ . For given values of  $L$ ,  $m$ , and  $V_0$  only certain energies  $E < V_0$  will satisfy Equation (12.3.5). Solutions to this equation are displayed in Figure 12.2.

In words, when we join the wave function of the particle trapped in the box to the wave function when it is in a region where  $E < V_0$ , there are only a few energies where the sinusoid of region 2 and the exponential of region 3 have the appropriate behavior at  $x = L/2$ . This implies that the allowed energies are quantized whenever  $E < V_0$ , i.e., for a classically trapped particle. The surprising result we've shown, however, is that quantum mechanics predicts a nonzero probability of finding the particle to the right of the barrier beyond  $x = L/2$  (and also to the left of the barrier at  $x = -L/2$ ).

In the case of the infinitely deep well where  $V = \infty$  outside of the box, solutions could be thought of as fitting an integral number of sine waves into a fixed width, hence energy quantization. Since most wavelengths do not fit inside the fixed width most energies are not allowed. In the case of a finite well, wave functions are allowed to leak past the barrier yet we still see energy quantization because not all solutions to the wave function on both sides of the barrier behave appropriately at the barrier. For some arbitrarily chosen total energy of a system  $E$ , the wave function in all regions of space depends on  $E$ . We can draw the wave functions at any point in space as well, however, only certain values of  $E$  guarantee that the sinusoid within a region of zero potential forms a smooth junction with the decaying exponential of a region of nonzero potential.

There are two important differences between the infinitely deep well and the finitely deep well:

1. There are a finite number of bound levels in a finitely deep well which depend on the energy of the system.

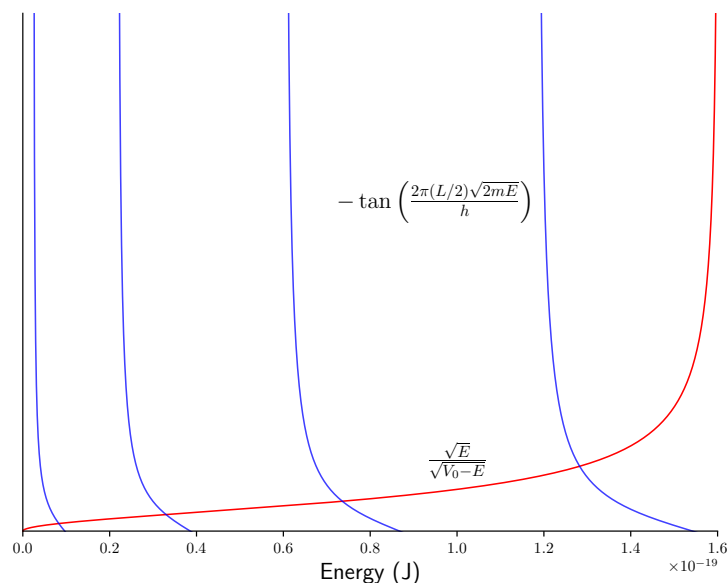


Figure 12.2: Graphical solutions to the allowed energies of a particle in a finite depth box. In blue is the tangent expression from Equation (12.3.5) and in red is the other side of the equation. Values for the relevant parameters are  $L = 2.50$  nm,  $m = 9.11 \times 10^{-31}$  kg, and  $V_0 = 1$  eV.

That is, the energy of the particle in a box remains quantized whether the box is infinitely deep or not.

2. The wave function at the edge of the box does not go to zero and instead extends into the classically forbidden region. The extent of penetration is dependent on the energy of the system and increases with increasing energy.

### 12.3.1 Two Finite Depth Boxes Interacting Through a Barrier

Oftentimes in chemistry and biology we consider molecules or systems which can have any one of several stable configurations. A simple example would be the geometry of ammonia, which prefers a trigonal pyramidal configuration. This geometry can be reached by one of two equivalent configurations: if the central axis of the molecule is located along the  $z$ -axis, the three hydrogen atoms can lie either below or above the  $xy$ -plane, with the lone pair on nitrogen lying to the other side. Both geometries are the most stable configuration yet there is a relatively large energy barrier between the configurations due to steric and electronic repulsion. Similarly, we might also cite Berry pseudorotation as an example. In this case, two stable trigonal bipyramidal geometries are separated by a high-energy planar intermediate.

In the classical mechanical treatment of two boxes separated by an energy barrier we would solve for the trajectory of a system trapped in one of any of the stable configurations and assert that the solution is the same for all other stable configurations and that solutions in one region are independent of solutions in another. That is, if a system exists in one stable configuration, it neither knows about nor would care about any other stable configurations. However, due to barrier penetration, the solutions to quantum mechanical systems are effected by the presence of equally stable configurations.

### 12.3.2 Quantum Tunneling

*Quantum tunneling* is the phenomenon whereby a wave function can propagate through a potential energy barrier, a process which is wholly forbidden in classical mechanics. Imagine a ball rolling up a hill: if the ball has an energy  $E > U_g$ , where  $U_g$  represents the gravitational potential energy at the top of the hill, it will roll over and reach the other side. Otherwise, if  $E < U_g$ , the ball will reflect from the energy barrier and roll

back down, never to be found on the other side of the hill. In contrast, when a quantum mechanical particle approaches an energy barrier there is a small probability of penetration into the classically forbidden region, as we've seen. In fact, if the energy of the wave function is large enough and the potential energy barrier short enough, the wave function may be found on the other side of the barrier! Although the wave function would have decreased within the barrier, it hasn't vanished when it reaches the other side.

This scenario is analogous to if the ball rolling up a hill described earlier, instead of rolling back down the hill, rolled straight *through* the hill when it reached the classical turning point. Although this is strictly forbidden in classical mechanics, it is acceptable behavior to quantum mechanical particles.

We'll now go on to derive the *transmission probability* of a particle in a box, that is, the probability a particle will tunnel completely through a potential energy barrier and reach the other side. Suppose that we have a particle defined on the following intervals with associated potential energies:

$$\begin{array}{lll} \text{Region 1} & V(x) = 0 & \text{for } x \leq 0 \\ \text{Region 2} & V(x) = V_0 & \text{for } 0 < x \leq L \\ \text{Region 3} & V(x) = 0 & \text{for } L < x \end{array}$$

We'll assume that the particle is bounded by an infinite potential somewhere less than zero so that it does not penetrate at all outside of the boundary at  $x = 0$  and  $x = L$ . Therefore, in region 1 we require that the wave function look something like that of our wave function for the finite barrier case, written  $\psi_1(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$  for constants  $A$ ,  $B$ , and  $\alpha$ .

The spatial component of the wave function must have the following form in each region if the energy of the particle at any point in space is less than the potential energy barrier  $V_0$ :

$$\begin{array}{lll} \psi_1(x) = Ae^{i\alpha x} + Be^{-i\alpha x} & \alpha = \sqrt{\frac{2mE}{\hbar^2}} & \text{Region 1} \\ \psi_2(x) = Ce^{-\beta x} + De^{\beta x} & \beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} & \text{Region 2} \\ \psi_3(x) = Fe^{i\alpha x} + Ge^{-i\alpha x} & & \text{Region 3} \end{array}$$

Assuming that the wave approaches the barrier from the negative  $x$  direction, i.e., interacting with the barrier at  $x = 0$  first, we can suppose that the coefficient  $B$  is nonzero since the term  $Be^{-i\alpha x}$  represent a reflection from the barrier. Similarly, the term  $Ge^{-i\alpha x}$  represents a reflection from the barrier in the positive  $x$  region, at  $x = L$ . In contrast to before, however, we aren't interested in this reflection and therefore allow  $G = 0$ .

By the differentiability of the wave function we know that at each barrier the wave must be smooth and continuous. That is,  $\psi_1(0) = \psi_2(0)$  and  $\frac{\partial}{\partial x}\psi_1(0) = \frac{\partial}{\partial x}\psi_2(0)$ . Similar statements can be made for the barrier at  $x = L$  and the wave functions  $\psi_2(x)$  and  $\psi_3(x)$ . Firstly, we'll concern ourselves with the barrier at  $x = 0$ :

$$\begin{aligned} \psi_1(0) = \psi_2(0) &\Rightarrow Ae^{i\alpha(0)} + Be^{-i\alpha(0)} = Ce^{-\beta(0)} + De^{\beta(0)} \\ A + B &= C + D \end{aligned} \tag{12.3.6}$$

$$\begin{aligned} \frac{\partial\psi_1(0)}{\partial x} = \frac{\partial\psi_2(0)}{\partial x} &\Rightarrow i\alpha Ae^{i\alpha(0)} - \alpha\alpha Be^{-i\alpha(0)} = -\beta Ce^{-\beta(0)} + \beta De^{\beta(0)} \\ i\alpha A - i\alpha B &= -\beta C + \beta D \\ A - B &= -\frac{i\beta}{\alpha}(-C + D) \end{aligned} \tag{12.3.7}$$

Equations (12.3.6) and (12.3.7) represent two conditions that the wave functions in regions 1 and 2 *must satisfy* in order for the energy of the wave function to be allowed. Now, we consider the boundary at  $x = L$ , invoking



the condition that  $G = 0$  as previously mentioned.

$$\psi_2(L) = \psi_3(L) \Rightarrow Ce^{-\beta L} + De^{\beta L} = Fe^{i\alpha L} \quad (12.3.8)$$

$$\begin{aligned} \frac{\partial \psi_2(L)}{\partial x} = \frac{\partial \psi_3(L)}{\partial x} &\Rightarrow -\beta Ce^{-\beta L} + \beta De^{\beta L} = i\alpha Fe^{i\alpha L} \\ -Ce^{-\beta L} + De^{\beta L} &= \frac{i\alpha}{\beta} Fe^{i\alpha L} \end{aligned} \quad (12.3.9)$$

Equations (12.3.8) and (12.3.9) represent two more conditions that the wave functions in regions 2 and 3 must satisfy in order for the energy of the wave function to be allowed.

At this point we may recognize that the *transmission probability* is given by the term  $|F/A|^2$ . Note that the term  $Ae^{i\alpha x}$  represents a wave incident to the barrier coming from the negative direction while the term  $Fe^{i\alpha x}$  represents a wave moving away from the barrier in the positive  $x$  direction. Therefore, we consider the ratio

$$\frac{FF^*}{AA^*} = \left| \frac{F}{A} \right|^2$$

to be the probability of the wave emerging on the other side of the barrier when coming in contact with it. It is useful to manipulate Equations (12.3.6) through (12.3.9) to get a relationship between  $F$  and  $A$ . By adding and subtracting the first pair of equations,  $A$  and  $B$  can be expressed in terms of  $C$  and  $D$ . The second pair of equations can be combined in the same way to give equations for  $C$  and  $D$  in terms of  $F$ . To acquire an expression for  $D$  we'll add together Equations (12.3.8) and (12.3.9):

$$\begin{aligned} Ce^{-\beta L} + De^{\beta L} + (-Ce^{-\beta L} + De^{\beta L}) &= Fe^{i\alpha L} + \left( \frac{i\alpha}{\beta} Fe^{i\alpha L} \right) \\ 2De^{\beta L} &= \frac{\beta}{\beta} Fe^{i\alpha L} + \frac{i\alpha}{\beta} Fe^{i\alpha L} \\ D &= \frac{i\alpha e^{i\alpha L} + \beta e^{i\alpha L}}{2\beta e^{\beta L}} F \end{aligned} \quad (12.3.10)$$

To acquire an expression for  $C$  we'll subtract Equation (12.3.9) from (12.3.8):

$$\begin{aligned} Ce^{-\beta L} + De^{\beta L} - (-Ce^{-\beta L} + De^{\beta L}) &= Fe^{i\alpha L} - \left( \frac{i\alpha}{\beta} Fe^{i\alpha L} \right) \\ 2Ce^{-\beta L} &= \frac{\beta}{\beta} Fe^{i\alpha L} - \frac{i\alpha}{\beta} Fe^{i\alpha L} \\ C &= \frac{-i\alpha e^{i\alpha L} + \beta e^{i\alpha L}}{2\beta e^{-\beta L}} F \end{aligned} \quad (12.3.11)$$

To acquire an expression for  $A$  we'll add Equations (12.3.6) from (12.3.7):

$$\begin{aligned} A + B + (A - B) &= C + D + \left( -\frac{i\beta}{\alpha} (-C + D) \right) \\ 2A &= \frac{\alpha C + \alpha D + i\beta C - i\beta D}{\alpha} \\ A &= \frac{i\alpha C + i\alpha D - \beta C + \beta D}{2i\alpha} \\ &= \frac{(i\alpha - \beta)C + (i\alpha + \beta)D}{2i\alpha} \end{aligned} \quad (12.3.12)$$

as desired. We can substitute Equations (12.3.10) and (12.3.11) into Equation (12.3.12) to obtain an expression

for  $A$  in terms of  $F$ :

$$\begin{aligned}
 A &= \frac{i\alpha - \beta}{2i\alpha} \left( \frac{-i\alpha e^{i\alpha L} + \beta e^{i\alpha L}}{2\beta e^{-\beta L}} F \right) + \frac{i\alpha + \beta}{2i\alpha} \left( \frac{i\alpha e^{i\alpha L} + \beta e^{i\alpha L}}{2\beta e^{\beta L}} F \right) \\
 &= \frac{e^{i\alpha L}}{2i\alpha(2\beta)} \left[ i\alpha - \beta \left( \frac{-i\alpha + \beta}{e^{-\beta L}} \right) + i\alpha + \beta \left( \frac{i\alpha + \beta}{e^{\beta L}} \right) \right] F \\
 2i\alpha A &= \frac{e^{i\alpha L}}{2\beta} \left[ (i\alpha - \beta)(-i\alpha + \beta)e^{\beta L} + (i\alpha + \beta)(i\alpha + \beta)e^{-\beta L} \right] F
 \end{aligned} \tag{12.3.13}$$

At this point we can take advantage of the functions hyperbolic sine and hyperbolic cosine with the associated identities

$$\sinh x = \frac{e^x - e^{-x}}{2}, \quad \text{and} \quad \cosh x = \frac{e^x + e^{-x}}{2}$$

and the relationship  $\cosh^2 x - \sinh^2 x = 1$ , to manipulate Equation (12.3.13) into a more functional form for the transmission probability. With a little bit of algebraic gymnastics we can show that

$$\begin{aligned}
 2i\alpha A &= \frac{e^{i\alpha L}}{2\beta} \left[ (i\alpha - \beta)(-i\alpha + \beta)e^{\beta L} + (i\alpha + \beta)(i\alpha + \beta)e^{-\beta L} \right] F \\
 \frac{A}{F} &= \frac{e^{i\alpha L}}{4i\alpha\beta} \left[ (-i^2\alpha^2 + 2i\alpha\beta - \beta^2)e^{\beta L} + (i^2\alpha^2 + 2i\alpha\beta + \beta^2)e^{-\beta L} \right] \\
 &= \frac{e^{i\alpha L}}{2i\alpha\beta} \left[ (\alpha^2 + 2i\alpha\beta - \beta^2) \frac{e^{\beta L}}{2} + (-\alpha^2 + 2i\alpha\beta + \beta^2) \frac{e^{-\beta L}}{2} \right] \\
 &= \frac{e^{i\alpha L}}{2i\alpha\beta} \left[ \alpha^2 \left( \frac{e^{\beta L} - e^{-\beta L}}{2} \right) + 2i\alpha\beta \left( \frac{e^{\beta L} + e^{-\beta L}}{2} \right) - \beta^2 \left( \frac{e^{\beta L} - e^{-\beta L}}{2} \right) \right] \\
 &= \frac{e^{i\alpha L}}{2i\alpha\beta} \left[ (\alpha^2 - \beta^2) \sinh(\beta L) + 2i\alpha\beta \cosh(\beta L) \right]
 \end{aligned}$$

Now we'll square this expression. Note that the absolute value bars imply multiplying this expression by its complex conjugate.

$$\begin{aligned}
 \left| \frac{A}{F} \right|^2 &= \left( \frac{e^{i\alpha L}}{2i\alpha\beta} \right) \left[ (\alpha^2 - \beta^2) \sinh(\beta L) + 2i\alpha\beta \cosh(\beta L) \right] \\
 &\quad \times \left( \frac{e^{-i\alpha L}}{2i\alpha\beta} \right) \left[ (\alpha^2 - \beta^2) \sinh(\beta L) - 2i\alpha\beta \cosh(\beta L) \right] \\
 &= \frac{1}{-4i^2\alpha^2\beta^2} \left[ (\alpha^2 - \beta^2)^2 \sinh^2(\beta L) - 4i^2\alpha^2\beta \cosh^2(\beta L) \right] \\
 &= \frac{1}{16\alpha^2\beta^2} \left[ 4(\alpha^2 - \beta^2)^2 \sinh^2(\beta L) + 16\alpha^2\beta^2 \cosh^2(\beta L) \right] \\
 &= \frac{1}{16\alpha^2\beta^2} \left[ 4(\alpha^2 - \beta^2)^2 \sinh^2(\beta L) + 16\alpha^2\beta^2 (1 + \sinh^2(\beta L)) \right] \\
 &= \frac{1}{16\alpha^2\beta^2} \left[ 16\alpha^2\beta^2 + (4(\alpha^2 - \beta^2)^2 + 16\alpha^2\beta^2) \sinh^2(\beta L) \right] \\
 \left| \frac{F}{A} \right|^2 &= \frac{16\alpha^2\beta^2}{16\alpha^2\beta^2 + (4(\alpha^2 - \beta^2)^2 + 16\alpha^2\beta^2) \sinh^2(\beta L)} \\
 &= \frac{16(\alpha\beta)^2}{16(\alpha\beta)^2 + (4(\alpha^2 - \beta^2)^2 + 16(\alpha\beta)^2) \sinh^2(\beta L)}
 \end{aligned} \tag{12.3.14}$$

which is the transmission probability.

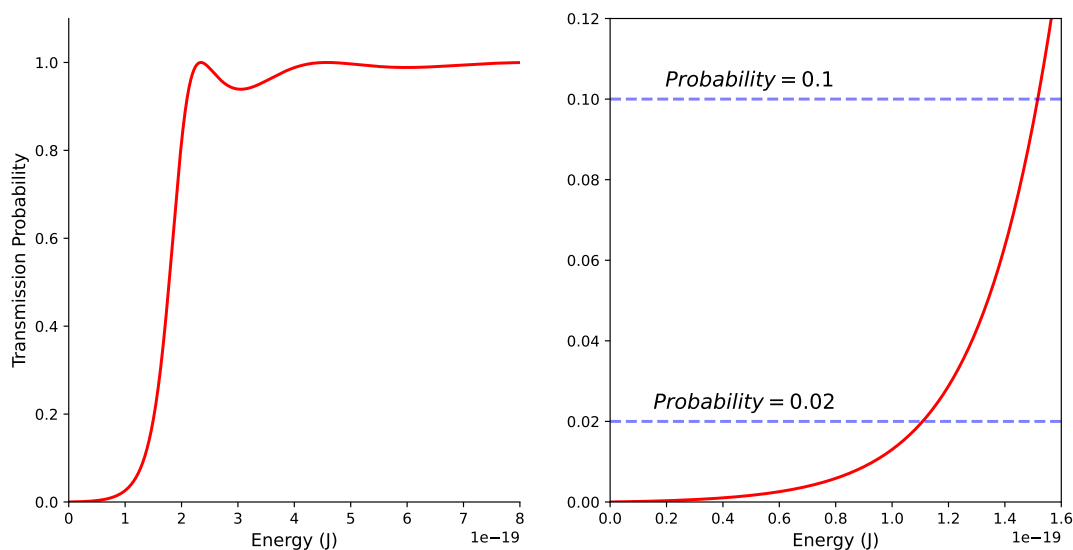


Figure 12.3: The transmission probability for an electron as a function of energy for  $V_0 = 1.6 \times 10^{-19}$  J and  $L = 9 \times 10^{-10}$  m up to an energy of  $8 \times 10^{-19}$  J. Both plots utilize Equation (12.3.14) and are shown for different window sizes. The transmission probabilities of 0.02 and 0.1 are given for reference.

### 12.3.3 Band Theory

Valence electrons on adjacent atoms in a molecule or solid can have appreciable overlap, as we've seen using the particle in a box method for a finite barrier. This implies that electrons can move between one atom from the next. If a large number  $N$  of identical atoms come together to form a crystal, such as  $\text{Na}_{(s)}$ , the overlap of atomic orbitals causes each discrete energy level to split into  $N$  energy levels, each of a different energy. Since the number of atoms in a macroscopic piece of solid is very large, the number of orbitals is incredibly large and thus they are closely spaced. The adjacent energy levels are so closely spaced that they can be considered a continuum, or an *energy band*.

A *band gap* can be thought of as the “leftover” energy levels which are not covered by the band, as a result of the finite width of bands. Figure 12.4 nicely illustrates this consequence and how it arises naturally from the interatomic distance of atoms in a crystal. Importantly, remember that although the graph illustrates how interatomic distance effects conductivity, what's most important is the overlap of high energy atomic orbitals.

Suppose that we consider the valence electrons of sodium metal. The 3s electron in sodium is weakly bound to the nucleus and therefore its ground state is fairly high-energy relative to the other electrons in the atom. As sodium atoms grow nearer to each other, the wave functions of the valence electron attain more significant overlap and the ground state energy of the valence electrons in each atom is greater than the potential energy between them. Figure 12.5 illustrates how adjacent sodium atoms allow electrons to delocalize and conduct electricity.

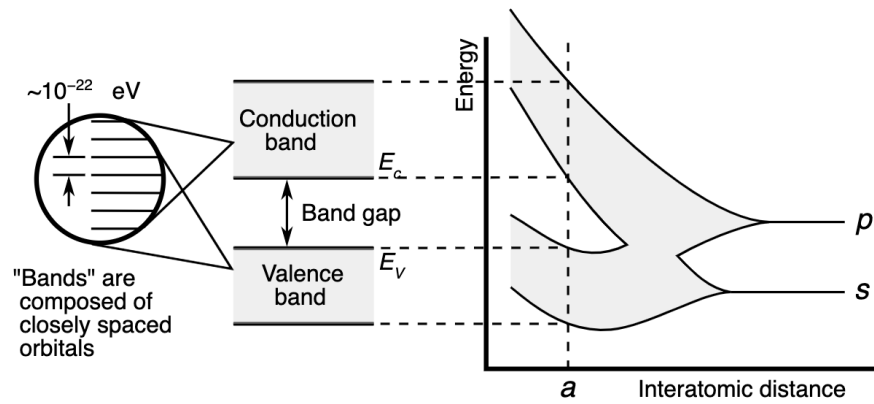


Figure 12.4: Illustration of how electronic band structure comes about in a large crystal of atoms. The graph to the right illustrates energy levels as a function of interatomic distance in diamond. When atoms are far apart, each carbon has valence  $p$  and  $s$  orbitals which have equal energy. When brought close enough together their orbitals begin to overlap and give rise to bands. Distance between valence and conduction band in diamond is 5.5 eV. At room temp, very few electrons attain the thermal energy necessary to surmount this gap, hence the reason why diamond does not conduct electricity.

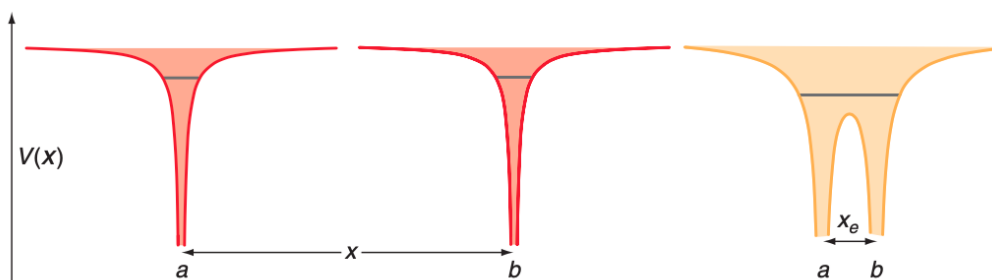


Figure 12.5: The overlap of electron wave function as two sodium atoms grow closer to one another.  $x_e$  represents the interatomic distance and the grey line through the wave function represents the zero-point energy of the valence electron. Since this energy is greater than the potential energy between the atoms the electron is allowed to delocalized and conduct electricity.

## CHAPTER

# 13

# UNCERTAINTY AND COMMUTATION RELATIONS

*Uncertainty*

- *Scientist*

Classical physics predicts that there is no limit to the amount of information that can be known about a system at a given instant of time. In other words, the exact value of all possible observables can be known and knowledge about the behavior of the system with time can be precisely determined. This is not the case in quantum mechanics.

*Uncertainty* limits the degree to which certain observables can be known simultaneously. Since the uncertainty principle is ubiquitous within quantum mechanics, numerous experiments have been conducted with and without the express purpose of illustrating this effect. A common method of determining if two observables can be simultaneously known measuring whether or not they *commute* using a commutator.

Importantly, *operators which commute share common eigenstates*, and can be simultaneously known.

## 13.1 Commutation Relations

The values for two different observables, say,  $a$  and  $b$ , which correspond to operators  $\hat{A}$  and  $\hat{B}$ , can be simultaneously determined if and only if the measurement process does not change the state of the system. Otherwise, the system on which the second measurement is made is not the same as if the same measurement had been made first.

Suppose that  $\psi$  represents a wave function and that  $\hat{A}$  and  $\hat{B}$  operate on  $\psi$  such that  $\psi$  is an eigenfunction of both operators. If we first operate on  $\psi$  with  $\hat{A}$  and then follow it up by operating with  $\hat{B}$  we'd expect that  $\hat{B}[\hat{A}\psi] = \hat{B}[a\psi] = a\hat{B}\psi$  since  $a$  is a constant. Similarly, since  $\psi$  is also an eigenfunction of  $\hat{B}$ , carrying out the operation with  $\hat{B}$  first would yield  $\hat{A}[\hat{B}\psi] = b\hat{A}\psi$ .

The only case in which  $\psi$  is an eigenfunction of both  $\hat{A}$  and  $\hat{B}$  is if the first measurement does not change the state of the system. In such a case, we'd expect that  $\hat{A}[\hat{B}\psi] = \hat{B}[\hat{A}\psi] = ab\psi$ . Thus, we conclude that the act of measurement changes the state of  $\psi$  unless  $\psi$  is an eigenfunction of both operators. *This is the condition*

for being able to simultaneously and precisely know the values of two observables. Determining whether or not  $\psi$  is an eigenfunction of two operators can therefore be done testing the relationship

$$\hat{A}[\hat{B}\psi] - \hat{B}[\hat{A}\psi] = 0 \quad (13.1.1)$$

which corresponds to  $\hat{A}[\hat{B}\psi] = \hat{B}[\hat{A}\psi]$ . If Equation (13.1.1) holds for two operators those operators are said to *commute*.

An incredibly useful application of commutators comes in the form of determining whether or not the angular momentum operators for a particle commute. Recall that the angular momentum for a particle takes the form  $\vec{l} = \vec{r} \times \vec{p}$  for the position and momentum vectors  $\vec{r}$  and  $\vec{p}$ . The angular momentum for each of the  $x$ ,  $y$ , and  $z$  directions can be determined by evaluating the cross product:

$$\begin{aligned} \vec{l} = \vec{r} \times \vec{p} &= \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= (yp_z - zp_y)\hat{i} - (xp_z - zp_x)\hat{j} + (xp_y - yp_x)\hat{k} = \vec{l}_x + \vec{l}_y + \vec{l}_z \end{aligned}$$

By substituting the position and momentum operators we can determine the corresponding angular momentum operators:

$$\begin{aligned} \hat{l}_x + \hat{l}_y + \hat{l}_z &= \left(-i\hbar y \frac{\partial}{\partial z} + i\hbar z \frac{\partial}{\partial y}\right) \hat{i} - \left(-i\hbar x \frac{\partial}{\partial z} + i\hbar z \frac{\partial}{\partial x}\right) \hat{j} + \left(-i\hbar x \frac{\partial}{\partial y} + i\hbar y \frac{\partial}{\partial x}\right) \hat{k} \\ &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \hat{i} - i\hbar \left(-x \frac{\partial}{\partial z} + z \frac{\partial}{\partial x}\right) \hat{j} - i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right) \hat{k} \end{aligned}$$

Now, we'll evaluate the commutator  $[\hat{l}_x, \hat{l}_y]$  on some arbitrary wave function  $\psi(x, y, z)$ :

$$\begin{aligned} [\hat{l}_x, \hat{l}_y] &= \hat{l}_x[\hat{l}_y\psi] - \hat{l}_y[\hat{l}_x\psi] \\ &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \left[-i\hbar \left(-x \frac{\partial}{\partial z} + z \frac{\partial}{\partial x}\right) \psi\right] + i\hbar \left(-x \frac{\partial}{\partial z} + z \frac{\partial}{\partial x}\right) \left[-i\hbar \left(-y \frac{\partial}{\partial z} + z \frac{\partial}{\partial y}\right) \psi\right] \\ &= -\hbar^2 \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}\right) \left[-x \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial x}\right] - \hbar^2 \left(-x \frac{\partial}{\partial z} + z \frac{\partial}{\partial x}\right) \left[-y \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial y}\right] \\ &= -\hbar^2 y \frac{\partial}{\partial z} \left[-x \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial x}\right] + \hbar^2 z \frac{\partial}{\partial y} \left[-x \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial x}\right] + \hbar^2 x \frac{\partial}{\partial z} \left[-y \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial y}\right] - \hbar^2 z \frac{\partial}{\partial x} \left[-y \frac{\partial \psi}{\partial z} + z \frac{\partial \psi}{\partial y}\right] \\ &= \left\{ \hbar^2 xy \frac{\partial^2 \psi}{\partial z^2} - \hbar^2 y \left( z \frac{\partial^2 \psi}{\partial x \partial z} + \frac{\partial \psi}{\partial x} \right) \right\} + \left\{ -\hbar^2 xz \frac{\partial^2 \psi}{\partial z \partial y} + \hbar^2 z^2 \frac{\partial^2 \psi}{\partial x \partial y} \right\} \\ &\quad - \left\{ \hbar^2 xy \frac{\partial^2 \psi}{\partial z^2} - \hbar^2 x \left( z \frac{\partial^2 \psi}{\partial y \partial z} + \frac{\partial \psi}{\partial y} \right) \right\} - \left\{ -\hbar^2 yz \frac{\partial^2 \psi}{\partial x \partial z} + \hbar^2 z^2 \frac{\partial^2 \psi}{\partial x \partial y} \right\} \\ &= \hbar^2 y \frac{\partial \psi}{\partial x} - \hbar^2 x \frac{\partial \psi}{\partial y} \\ &= -\hbar^2 \left( x \frac{\partial \psi}{\partial y} - y \frac{\partial \psi}{\partial x} \right) \\ &= -(i\hbar \times i\hbar) \hat{l}_z \psi = i\hbar \hat{l}_z \psi \end{aligned}$$

Thus, we see that the operators  $\hat{l}_x$  and  $\hat{l}_y$  do not commute. A more rigorous derivation of this relationship can be done using matrix representations for operators, though, we don't really care about that.

The cyclic relations of commutations between angular momentum operators is fairly intuitive:

$$\begin{aligned}[\hat{l}_x, \hat{l}_y] &= i\hbar\hat{l}_z \\ [\hat{l}_x, \hat{l}_z] &= i\hbar\hat{l}_y \\ [\hat{l}_y, \hat{l}_z] &= i\hbar\hat{l}_x\end{aligned}$$

## 13.2 The Uncertainty Principle

The *uncertainty principle* is a quantum mechanical result that asserts a fundamental limit to the accuracy with which pairs of physical quantities can be measured. The most famous of these, the *Heisenberg uncertainty principle*, relates the uncertainty in a particle's position to its momentum such that

$$\sigma_x \sigma_p \geq \frac{\hbar}{2} \quad (13.2.1)$$

where  $\sigma_x$  and  $\sigma_p$  are the respective standard deviations in the position and momentum which have the same meaning as uncertainty.

Pairs of variables which satisfy this inequality are known as *complementary* or *conjugate variables*. In classical physics, conjugate variables are found by considering the *action* of a system, which is a numerical value describing how a system changes over time.<sup>1</sup> The action of a system has units of joule-seconds; products of quantities which afford these units include energy  $\times$  time or momentum  $\times$  length. Action relates to conjugate variables because the *derivatives of action with respect to some variable is conjugate to the variable with which we are differentiating*. I know, that doesn't immediately make a ton of sense. So, consider the example of the conjugate variables length and momentum. In this case, action =  $px$  for the momentum  $p$  and length  $x$  and therefore

$$\frac{d(\text{action})}{dx} = p \quad \text{or} \quad \frac{d(\text{action})}{dp} = x$$

So,  $x$  and  $p$  are conjugate variables. While we are analyzing conjugate pairs of variables using classical mechanics, these same pairs are related via the uncertainty principle. More common examples include,

- The change in *energy* of a particle and the *time* it takes for the change to occur
- The *angular momentum* of a particle and its *orientation*, or *angular position*
- The *electric potential* and the negative *free electric charge* of some event

among others.<sup>2</sup> The uncertainty relation between energy and time is a consequential one. Consider the energy of an electron in hydrogen in the 1s state. The energy of this electron is known very precisely because the lifetime of an electron in this state is very long, since it's the ground state. Excited state which decay rapidly, in the case of hydrogen those might be the 2s, 2p, or 3s shells, have more uncertainty in their energy since the lifetime of an electron in that state is much shorter.

Most generally, the uncertainty principle of quantum mechanics is related by the commutator of two operators:

$$\sigma_A \sigma_B \geq \frac{1}{2} [\hat{A}, \hat{B}] \quad (13.2.2)$$

Here, we are assuming that the operators  $\hat{A}$  and  $\hat{B}$  do not commute.

<sup>1</sup>Action is significant because the equations of motion for a system, whether we consider Newtonian, Hamiltonian, or Lagrangian mechanics, can all be derived through the principle of least action. For our purposes, however, we only need to know how to calculate it.

<sup>2</sup>Conjugate variables are also *Fourier transforms* of one another, a consequence of *Fourier's theorem*, which is exceedingly intertwined with any discussion regarding waves and periodic functions.

This principle can be nicely illustrated with a free particle. The most general form of a periodic wave function for a free particle may be written

$$\Psi(x, t) = Ae^{i(kx - \omega t - \phi)}$$

for some constant  $A$ , a wave vector  $k = 2\pi/\lambda$ , an angular frequency  $\omega = 2\pi\nu$ , and phase angle  $\phi$ . For convenience, we'll allow  $t = 0$  and  $\phi = 0$  so that we consider only the spatial variation,  $\psi(x)$ . Firstly, we'll ensure that  $\psi(x)$  is normalized over some arbitrary finite interval:

$$\begin{aligned} \int_{-a}^a \int_{-a}^a \psi^*(x)\psi(x)dx &= \int_{-a}^a \int_{-a}^a A^* e^{-ikx} A e^{ikx} dx \\ &= |A|^2 \int_{-a}^a \int_{-a}^a dx \\ &= 2a|A|^2 \end{aligned}$$

Thus, the normalization constant for  $\psi(x)$  along this interval is  $A = 1/\sqrt{2a}$ . Note that although we're considering the wave function across some fixed interval  $-a < x < a$ , we *are not* confining the particle to this interval. Instead, normalizing the wave function over this specific interval allows us to compute relevant probabilities along  $-a < x < a$ . Now, if we consider the probability of finding the particle on some finite width  $dx$  centered at  $x = x_0$ , by Equation (11.2.1) from the postulates of quantum mechanics we have that

$$P(x_0)dx = \psi^*(x_0)\psi(x_0)dx = \frac{dx}{2a}$$

is the probability. Importantly, this probability is independent of position. Recall that the wave function we considered was that of a free particle such that  $a \rightarrow \infty$ . Thus, the probability of finding the particle anywhere, i.e., knowing the particle's position, is zero. Additionally, note that we can operate on  $\psi(x)$  with the momentum operator to afford  $\hat{p}\psi(x) = \hbar k$ . This implies that *the momentum is known exactly*. Thus, we've seen that being able to measure the momentum of a particle exactly necessarily implies that we know absolutely nothing about the position.

### 13.2.1 The Uncertainty Principle in Terms of Standard Deviations

Uncertainty, from a statistical perspective, is quantified by the standard deviation of a distribution. The standard deviation is defined as

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 \quad (13.2.3)$$

where  $\langle x \rangle$  is the average value of some variable.  $x$  could be the position, momentum, or energy of a particle. The nice things about averages is that if we know the wave function for some quantum mechanical particle we can compute the average value of any physical observable by the postulates of quantum mechanics.

For example, consider the wave function for the particle in a one-dimensional box of length  $a$ :

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right), \quad n = 1, 2, 3, \dots$$

Recall from Equation (11.2.8) that we can determine the average value of a physical observable by the equation

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{A} \psi(x) dx$$

where  $\psi(x)$  is assumed to be normalized. Using this equation we can determine the averages of the position and



momentum, as well as the second moment of each observable. I'll note that taking advantage of the symmetry of functions is *highly* useful in saving time while evaluating some of these integrals.

$$\begin{aligned}
 \langle x \rangle &= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \hat{x} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{n\pi x}{a}\right) dx \\
 &= \frac{2}{a} \int_0^a x \left[ \frac{1}{2} - \frac{1}{2} \cos\left(\frac{2n\pi x}{a}\right) \right] dx = \frac{2}{a} \int_0^a \frac{x}{2} - \frac{x}{2} \cos\left(\frac{2n\pi x}{a}\right) dx \\
 &= \frac{2}{a} \int_0^a \frac{x}{2} dx = \frac{2}{a} \left[ \frac{x^2}{4} \right]_0^a = \frac{a}{2}
 \end{aligned} \tag{13.2.4}$$

$$\begin{aligned}
 \langle x^2 \rangle &= \frac{2}{a} \int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a} \int_0^a x^2 \left[ \frac{1}{2} - \frac{1}{2} \cos\left(\frac{2n\pi x}{a}\right) \right] dx \\
 &= \frac{2}{a} \int_0^a \frac{x^2}{2} - \frac{x^2}{2} \cos\left(\frac{2n\pi x}{a}\right) dx \\
 &= \frac{2}{a} \left\{ \int_0^a \frac{x^2}{2} dx - \frac{1}{2} \left( \left[ \frac{ax^2 \sin\left(\frac{2n\pi x}{a}\right)}{4n\pi} \right]_0^a - \int_0^a \frac{2ax \sin\left(\frac{2n\pi x}{a}\right)}{2n\pi} dx \right) \right\} \\
 &= \frac{2}{a} \left\{ \left[ \frac{x^3}{6} \right]_0^a + \frac{a}{2n\pi} \int_0^a x \sin\left(\frac{2n\pi x}{a}\right) dx \right\} \\
 &= \frac{2}{a} \left\{ \frac{a^3}{6} + \frac{a}{2n\pi} \left( \left[ -\frac{ax \cos\left(\frac{2n\pi x}{a}\right)}{2n\pi} \right]_0^a + \int_0^a \frac{a \cos\left(\frac{2n\pi x}{a}\right)}{2n\pi} dx \right) \right\} \\
 &= \frac{2}{a} \left\{ \frac{a^3}{6} + \frac{a}{2n\pi} \left( -\frac{a^2}{2n\pi} \right) \right\} = \frac{2}{a} \left\{ \frac{a^3}{6} - \frac{a^3}{4n^2\pi^2} \right\} \\
 &= a^2 \left\{ \frac{1}{3} - \frac{1}{2n^2\pi^2} \right\}
 \end{aligned} \tag{13.2.5}$$

Using Equations (13.2.4) and (13.2.5) we can compute the standard deviation for the position of the particle in a box as

$$\begin{aligned}
 \sigma_x &= \sqrt{a^2 \left\{ \frac{1}{3} - \frac{1}{2n^2\pi^2} \right\} - \left( \frac{a}{2} \right)^2} \\
 &= a \sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}
 \end{aligned}$$

Now we follow an identical procedure for determining the uncertainty in the momentum for the particle in a box:

$$\begin{aligned}
 \langle p \rangle &= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \hat{p} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \left[ -i\hbar \frac{\partial}{\partial x} \sin\left(\frac{n\pi x}{a}\right) \right] dx \\
 &= \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \left[ -\frac{i\hbar n\pi}{a} \cos\left(\frac{n\pi x}{a}\right) \right] dx \\
 &= -\frac{2i\hbar n\pi}{a^2} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \cos\left(\frac{n\pi x}{a}\right) dx = 0
 \end{aligned} \tag{13.2.6}$$

$$\begin{aligned}
 \langle p^2 \rangle &= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \hat{p}^2 \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) dx = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right) \left[ -\hbar^2 \frac{\partial^2}{\partial x^2} \sin\left(\frac{n\pi x}{a}\right) \right] dx \\
 &= \frac{2\hbar^2 n^2 \pi^2}{a^3} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx \\
 &= \frac{2\hbar^2 n^2 \pi^2}{a^3} \int_0^a \left[ \frac{1}{2} - \frac{1}{2} \cos\left(\frac{2n\pi x}{a}\right) \right] dx \\
 &= \frac{2\hbar^2 n^2 \pi^2}{a^3} \left[ \frac{x}{2} - \frac{a}{4n\pi} \sin\left(\frac{2n\pi x}{a}\right) \right]_0^a \\
 &= \frac{\hbar^2 n^2 \pi^2}{a^2}
 \end{aligned} \tag{13.2.7}$$

Equations (13.2.6) and (13.2.7) allow us to find the standard deviation of the momentum for the particle in a box:

$$\begin{aligned}\sigma_p &= \sqrt{\frac{\hbar^2 n^2 \pi^2}{a^2} - (0)^2} \\ &= \frac{\hbar n \pi}{a}\end{aligned}$$

The Heisenberg uncertainty principle asserts that the product of the uncertainties in position and momentum should be greater than or equal to  $\hbar/2$ , from Equation (13.2.1). So, let's test this for our results above using the ground state,  $n = 1$ :

$$\sigma_x \sigma_p = \left( a \sqrt{\frac{1}{12} - \frac{1}{2n^2 \pi^2}} \right) \left( \frac{\hbar n \pi}{a} \right) = \hbar \sqrt{\frac{n^2 \pi^2}{12} - \frac{1}{2}} \approx 0.57 \hbar > \frac{1}{2} \hbar$$

Awesome! Our model for the particle in a box isn't breaking any physical laws, which is good. Note that the product of the uncertainties is slightly greater than  $\hbar/2$ , emphasizing that the uncertainty principle places a *lower bound* on what we can simultaneously know about two physical quantities.

### 13.2.2 The Size of an Atom

One important application of the uncertainty principle is in determining the size of atoms. Recall that from the perspective of classical physics, atoms should not exist because we expect electrons to spiral into the nucleus. If this were the case, electrons would have a definite position and momentum: situated at the nucleus with no momentum whatsoever. Clearly this is at odds with the uncertainty principle. Therefore, it must be the case that an electron can spiral into the nucleus no further than what is consistent with the uncertainty principle.

Consider the hydrogen atom. Here, the electron is trapped in some potential energy well due to the positive charge of the nucleus. Suppose that the electron is confined to some spherical shell about the nucleus of radius  $r$  so that its position may be uncertain up to the radius  $r$  in all of the  $x$ ,  $y$ , and  $z$  directions. Similarly, the  $x$ ,  $y$ , and  $z$  components of the momentum, denoted  $p_x$ ,  $p_y$ , and  $p_z$ , will be equal; by symmetry, the momentum in each direction is equally likely to be uncertain in either direction so that the uncertainty, say, in the  $x$  direction, is  $\Delta p_x \approx p$ .

By the Heisenberg uncertainty principle,  $\Delta x \Delta p_x \approx \hbar$  (and similarly for the  $y$  and  $z$  components) with  $\Delta x \approx r$  and  $\Delta p_x \approx p$ . This implies that  $\Delta p_x \approx p \approx \frac{\hbar}{r}$  and therefore the kinetic energy of the particle becomes

$$T = \frac{p^2}{2m_e} \approx \frac{\hbar^2}{2m_e r^2}$$

Including the coulombic potential of the electron,  $V = \frac{k q_e q_p}{r} = -\frac{q_e^2}{4\pi\epsilon_0 r}$ ,<sup>3</sup> the total energy of an electron in the hydrogen atom becomes

$$E = T + V \approx \frac{\hbar^2}{2m_e r^2} - \frac{q_e^2}{4\pi\epsilon_0 r} \quad (13.2.8)$$

Using Equation (13.2.8) we can determine the minimum energy of an electron in a hydrogen atom as a function of the distance between the electron and the nucleus. This is done by allowing the derivative of the

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<sup>3</sup>This is just a result of classical physics.  $q_p$  and  $q_e$  are the respective charges of a proton and an electron with  $q_p = -q_e$ .

total energy with respect to the radial distance between the electron and nucleus to be zero:

$$\begin{aligned}\frac{\partial E}{\partial r} &\approx \frac{\partial}{\partial r} \left[ \frac{\hbar^2}{2m_e r^2} - \frac{q_e^2}{4\pi\epsilon_0 r} \right] \\ 0 &= -\frac{\hbar^2}{m_e r^3} + \frac{q_e^2}{4\pi\epsilon_0 r^2} \\ \frac{\hbar^2}{m_e r} &= \frac{q_e^2}{4\pi\epsilon_0} \\ r &\approx \frac{4\pi\epsilon_0 \hbar^2}{m_e q_e^2} \approx 5.28 \times 10^{-11} \text{ m}\end{aligned}$$

Plugging this result back into Equation (13.2.8) affords the ionization energy for the electron in a hydrogen atom:

$$\begin{aligned}E &\approx \frac{\hbar^2}{2m_e \left( \frac{4\pi\epsilon_0 \hbar^2}{m_e q_e^2} \right)^2} - \frac{q_e^2}{4\pi\epsilon_0 \left( \frac{4\pi\epsilon_0 \hbar^2}{m_e q_e^2} \right)} \\ &\approx \frac{m_e q_e^4}{8\epsilon_0^2 \hbar^2} - \frac{m_e q_e^4}{16\epsilon_0^2 \hbar^2} \\ &\approx -\frac{m_e q_e^4}{8\epsilon_0^2 \hbar^2} \\ &\approx -13.61 \text{ eV}\end{aligned}$$

which agrees with the known ionization energy for the electron in a hydrogen atom.

### 13.3 The Stern-Gerlach Experiment

The *Stern-Gerlach experiment* demonstrated that the angular momentum of an electron is quantized and is one of the most direct pieces of evidence of quantization in quantum mechanics. In particular, the experiment represents a direct measurement of one component of the spin of an electron.

Before analyzing this experiment we'll recall some results from classical mechanics. The angular momentum of a particle is defined as

$$\vec{L} = \vec{r} \times \vec{p} \quad (13.3.1)$$

where  $\vec{r}$  and  $\vec{p}$  are the position and momentum vectors, respectively, and the angular momentum vector  $\vec{L}$  is defined as their cross product. Oftentimes,  $\vec{L}$  is referred to as the *orbital angular momentum*, since it is an important consideration in describing the properties of a particle orbiting around some center of attraction. In classical mechanics there is no restriction on the magnitude or direction of  $\vec{L}$ .

Because an electron carries an intrinsic charge, its (classical) angular momentum will result in a magnetic field whose strength is measured by the *magnetic moment*,  $\vec{\mu}$ , related to the orbital angular momentum by

$$\vec{\mu} = \frac{q_e}{2m_e} \vec{L}$$

for the respective charge and mass of an electron,  $q_e$  and  $m_e$ . Through experimentation, however, the quantum mechanical *spin* magnetic momentum is found to be

$$\vec{\mu}_S \approx -\frac{2q_e}{2m_e} \vec{S} = -\frac{q_e}{m_e} \vec{S} \quad (13.3.2)$$

where  $\vec{S}$  is the spin angular momentum vector of an electron.<sup>4</sup>

The experiment itself is setup as follows. A beam of silver atoms having a well-defined direction passes through a magnetic field that has a constant value in the  $xy$ -plane and varies linearly with  $z$  such that  $E(z) \sim z$  for the electric field  $E$ . The silver atoms pass through the magnetic field and are detected some distance beyond the magnetic which is arbitrary for the time being. The reason silver was used in this experiment was because a silver atom has a single lone electron which has an intrinsic magnetic moment (the property of electrons having a magnetic moment was unknown before the Stern-Gerlach experiment).

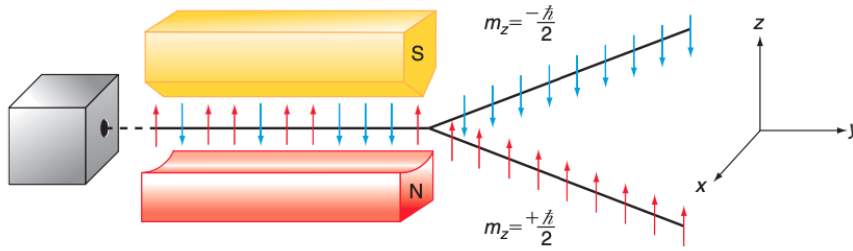


Figure 13.1: The apparatus in the Stern-Gerlach experiment. A beam of silver atoms is directed in the  $y$ -direction through a magnetic field that varies linearly with  $z$ . Consequently, the beam is directed in *only* the  $z$ -direction.

The results of this experiment illustrated that silver atoms were reflected in *only* the  $z$ -direction and that only two displacements in the  $z$  direction were observed: the displacement corresponding to an upward deflection and the displacement corresponding to the downward deflection, both of which had the same magnitude. Thus, the electron in silver must have some sort of magnetic moment since it reacts to the external magnetic field. In particular, the measured displacement corresponded to the lone electron in silver having a spin-magnetic moment of

$$\mu_z = \pm \mu_B = \pm \frac{q_e \hbar}{2m_e} \quad (13.3.3)$$

where  $\mu_B$  is the *Bohr magneton* and  $q_e$  is the charge of an electron. If we consider Equation (13.3.2), we see that in order for the magnetic moment in Equation (13.3.3) to correspond to that experimentally determined in Equation (13.3.2), the magnitude of the spin vector  $\vec{S}$  must be

$$S = \pm \frac{\hbar}{2}$$

which makes sense since electrons are spin- $\frac{1}{2}$  particles (a result from physics that we don't particularly care about but is good to know). In classical mechanics, we would expect the magnetic moment to take on any real value and therefore any displacement in the  $z$  direction would have been possible. Clearly, this is not what we've observed.

What conclusions can be drawn from this result? If we suppose that an operator  $\hat{S}$  exists which operates on a silver atom to measure its magnetic moment, we conclude that only two eigenvalues (and two corresponding eigenfunctions) exist for the operator which differ only in sign. We'll call these two eigenfunctions  $\psi_+$  and  $\psi_-$  and assume that they're properly normalized. Note that since these two eigenfunctions represent all possible observables in this experiment they form a complete set of all possible eigenfunctions of the system and therefore any linear combination of  $\psi_+$  and  $\psi_-$  yields another valid eigenfunction for the operator  $\hat{S}$ . So, the most general

<sup>4</sup>The approximation in Equation (13.3.2) is because the spin angular momentum is more formally defined as

$$\vec{\mu}_S = -\frac{q_e g}{2m_e} \vec{S}$$

where  $g$  is the *gyromagnetic ratio*. In classical mechanics  $g \approx 1$  but for an electron,  $g \approx 2$ .

solution to the (spatial) wave function corresponding to the electrons in a silver atom in this beam which is an eigenfunction of  $\hat{S}$  may be written

$$\Psi_S(x) = c_1\psi_+(x) + c_2\psi_-(x) \quad \text{with } |c_1|^2 + |c_2|^2 = 1 \quad (13.3.4)$$

I'm gonna make a brief aside. We know that the coefficients of Equation (13.3.4) must satisfy the equality  $|c_1|^2 + |c_2|^2 = 1$  by the orthogonality of eigenfunctions and normalization condition of the wave function. Since  $\psi^*(x)\psi(x)dx$  represents a probability,

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)dx \\ &= \int_{-\infty}^{\infty} (c_1\psi_+^*(x) + c_2\psi_-^*(x))(c_1\psi_+(x) + c_2\psi_-(x))dx \\ &= \int_{-\infty}^{\infty} (|c_1|^2\psi_+^*(x)\psi_+(x) + c_1c_2^*\psi_+(x)\psi_-^*(x) + c_1^*c_2\psi_+^*(x)\psi_-(x) + |c_2|^2\psi_-^*(x)\psi_-(x))dx \\ &= \int_{-\infty}^{\infty} |c_1|^2|\psi_+(x)|^2dx + \int_{-\infty}^{\infty} |c_2|^2|\psi_-(x)|^2dx \\ &= |c_1|^2 + |c_2|^2 \end{aligned}$$

which agrees with the result asserted previously.

A similar argument may be made for the operator which measures the magnetic moment in any one of the  $x$ ,  $y$ , or  $z$  directions. What we will inevitably find is that *none of these operators commute*. That is, we can never know the spin-magnetic moment of an electron in any two directions simultaneously. Consider the experimental setup in Figure 13.2. Here, a beam of silver atoms is shot through three different Stern-Gerlach devices, the first and last of which measure the spin-magnetic moment in the  $z$  direction and the second of which measures it in the  $x$  direction.

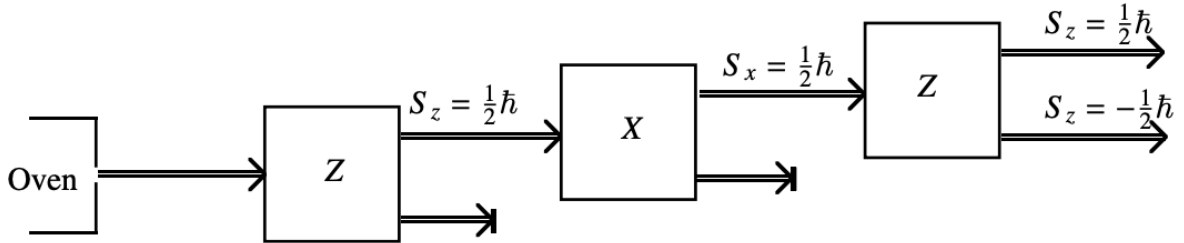


Figure 13.2: A series of measurements carried out using three Stern-Gerlach devices. The “oven” emits a beam of silver atoms and each box measures the spin-magnetic moment with respect to its label, i.e., the box labeled “Z” measures the spin-magnetic moment in the  $z$  direction.

After the beam passes through the first device, the spin-magnetic moment in the  $z$  direction is measured (to be  $+\frac{1}{2}\hbar$ , in this case). Then, the beam passes through the second device which measures the spin-magnetic moment in the  $x$  direction. From the perspective of classical physics, if we operated on the beam of silver atoms again with  $\hat{S}_z$ , that is, measured the spin-magnetic moment in the  $z$  direction, we’d expect the same result as if we had never operated on the beam with  $\hat{S}_x$ . This is not the case! Instead, operating on the beam with  $\hat{S}_z$  results in a distribution of spins identical to if we had zero information about the system to begin with.

I think that this is a great example because it illustrates two things. Firstly, the loss of information (or the *uncertainty*, as it were) when trying to measure two physical quantities which do not commute. Although the beam of atoms entering the Stern-Gerlach device which operates with  $\hat{S}_x$  in Figure 13.2 is “prepared” in the

$S_z = \frac{1}{2}\hbar$  state, after operating on the beam with  $\hat{S}_x$  its as if no information about the beam of atoms was known to begin with. Secondly, it reinforces the point that the only physical observables of a quantum mechanical system that can ever be measured are those which are eigenvalues of some operator. Sure, operating on the beam of atoms with  $\hat{S}_x$  removes any information we had previously attained about the spin-magnetic moment in the  $z$  direction, however, we always know that the only possible values of the spin-magnetic moment in the  $z$  direction will be  $\pm\frac{1}{2}\hbar$ .

## CHAPTER

# 14

# VIBRATIONS AND ROTATIONS OF QUANTUM MECHANICAL PARTICLES

*Vibrations*

- *Scientist*

A molecule is capable of having electronic, translational, rotational, and vibrational energy states, each of which is described by its own energy spectrum and eigenfunctions. As we've seen, the particle in a box is a useful model for discussing the allowed energies for translational degrees of freedom. Now, we consider the *harmonic oscillator* to explore vibrational degrees of freedom, followed by looking at a *rigid rotor* to analyze the effects of rotational freedoms on the energy of a molecule.

## 14.1 Classical Harmonic Oscillator

In any general physics class you've probably found solutions to the position of a harmonic oscillator (using a simple spring as a model) as a function of time using *Hooke's law*,  $F = -kx$  for some force constant  $k$  and displacement from the equilibrium position  $x$ . In the simplest case where the oscillator is fixed on one end and has some object of mass  $m$  on the other end, solutions are readily found. When the harmonic oscillator is allowed the freedom to move on either end, such as in the case of a diatomic molecule like HF or OH<sup>-</sup>, however, the location of each mass change differently with time and Hooke's law must be rewritten.

To model this scenario we can take advantage of the *reduced mass*, defined as

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (14.1.1)$$

where  $m_1$  and  $m_2$  are the masses of the objects on either end of the oscillator. Using the reduced mass allows us to transform a two-body problem into a one-body problem, which is much easier to solve; Hooke's law becomes  $F = -k\mu$  for the reduced mass and as we'll come to learn, in almost every case we can substitute  $\mu$  for  $m$  in any classical equation of motion to yield a corresponding equation of motion which concerns two bodies.

Now we can go about solving for the trajectory of a two-body harmonic oscillator as a function of time using the reduced mass and Hooke's law:

$$\begin{aligned} F &= \mu a = -kx \\ \frac{d^2x}{dt^2} &= -\frac{k}{\mu}x \\ \Rightarrow x(t) &= c_1 \cos\left(\sqrt{\frac{k}{\mu}}t\right) + c_2 \sin\left(\sqrt{\frac{k}{\mu}}t\right) \end{aligned}$$

A more detailed picture of how to solve differential equations of this form can be found in Appendix ???. If we restrict solutions to  $x(t)$  to the initial conditions  $x(0) = 0$  and  $v(0) = v_0$  (the initial velocity), the specific solution to the trajectory of this oscillator becomes

$$\begin{aligned} x(0) &= c_1 \cos\left(\sqrt{\frac{k}{\mu}} \times 0\right) + c_2 \sin\left(\sqrt{\frac{k}{\mu}} \times 0\right) = c_1 = 0 \\ v(0) &= -c_1 \sin\sqrt{\frac{k}{\mu}}\left(\sqrt{\frac{k}{\mu}} \times 0\right) + c_2 \sqrt{\frac{k}{\mu}} \cos\left(\sqrt{\frac{k}{\mu}} \times 0\right) = c_2 \sqrt{\frac{k}{\mu}} = v_0 \end{aligned}$$

Thus,

$$x(t) = v_0 \sqrt{\frac{\mu}{k}} \sin\left(\sqrt{\frac{k}{\mu}}t\right)$$

is the general solution to the two-body harmonic oscillator.

We can determine the period and frequency of the oscillator as follows: Since the sine function has a period of  $2\pi$ , it must be the case that

$$2\pi = \sqrt{\frac{k}{\mu}}(t + T) - \sqrt{\frac{k}{\mu}}t$$

where  $T$  is the period of oscillation and  $t$  is an arbitrarily chosen time. This affords the condition  $T = 2\pi\sqrt{\frac{\mu}{k}}$  and therefore the linear frequency of oscillation is  $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ . This allows us to rewrite the specific solution to the harmonic oscillator as

$$x(t) = b_1 \sin(\omega t) \tag{14.1.2}$$

where  $\omega = \sqrt{\frac{k}{\mu}}$  is the angular frequency and  $b_1 = v_0 \sqrt{\frac{\mu}{k}}$  is the amplitude.

Having supplanted an mathematical description of motion for the harmonic oscillator, we can test the physicality of our solution by considering the energy of the system. Recall that the kinetic energy of a body is given by (and substituting the reduced mass for a single mass),  $T = \frac{1}{2}\mu v^2$  and that the potential energy can be found via the relation  $F = -\frac{\partial V}{\partial x}$  to afford  $U = \frac{1}{2}kx^2$ . Thus, the total energy of the system is given by

$$E = T + V = \frac{1}{2}\mu v^2 + \frac{1}{2}kx^2$$

Because there are no constraints on the displacement length or velocity of the oscillator, the energy spectrum for a classical oscillator is *continuous*. Plugging in our result for the trajectory of the system in Equation



(14.1.2),

$$\begin{aligned}
E &= \frac{1}{2}\mu (b_1\omega \cos(\omega t))^2 + \frac{1}{2}k (b_1 \sin(\omega t))^2 \\
&= \frac{1}{2}\mu b_1^2\omega^2 \cos^2(\omega t) + \frac{1}{2}k b_1^2 \sin^2(\omega t) \\
&= \frac{1}{2}\mu b_1^2\omega^2 \cos^2(\omega t) + \frac{1}{2}\mu\omega^2 b_1^2 \sin^2(\omega t) \\
&= \frac{1}{2}\mu b_1^2\omega^2
\end{aligned} \tag{14.1.3}$$

which is the total energy of the oscillator with each constant defined previously. Above I took advantage of the relationship  $k = \mu\omega^2$  to make factoring easier. Notice that this expression is independent of time, exactly as we would expect for a system which is not exchanging energy with its surroundings.

Following a similar procedure for a quantum mechanical oscillator, we'll see that the energy spectrum follows a discrete spectrum (potentially unsurprisingly). The analysis performed here for a classical harmonic oscillator will allow us to compare and contrast the results across the classical and quantum views of mechanics.

### 14.1.1 Probability Density for a Classical Harmonic Oscillator

The *classical probability density* for a harmonic oscillator represents the likelihood of finding a particle near a certain location subject to some potential energy function. This probability density will be helpful in gaining insight into the correspondence principle and making connections between classical and quantum mechanics.

If we consider a harmonic oscillator with a trajectory modeled by Equation (14.1.2), the position where the particle is most likely to be found will be directly proportional to the amount of time spent at that position. For example, in regions of high velocity (near the equilibrium position), the particle will spend very little time and therefore is unlikely to be found there at any given instant. In contrast, at the classical turning points (regions of maximal amplitude), the particle has very little kinetic energy and spends more time in the region and therefore is more likely to be found there at any given instant. Representing the probability density as  $P(x)$ , this corresponds to the relation

$$P(x)dx \propto dt \tag{14.1.4}$$

for some differential changes in position and time,  $dx$  and  $dt$ . As we've seen, the motion of this oscillator is periodic so that the displacement of an object is bounded below and on top and therefore the density can be properly normalized for some normalization constant  $N$ :

$$\int_{x_{\min}}^{x_{\max}} P(x)dx = N \int_{t_0}^{t_0+T/2} dt = 1$$

Above,  $x_{\min}$  and  $x_{\max}$  correspond to the amplitudes (in the negative and positive directions, respectively),  $t_0$  is some arbitrarily chosen time, and  $T$  is the period of oscillation.

Note that the oscillator travels from  $x_{\min}$  to  $x_{\max}$  *within half of a period*; a full period of oscillation corresponds to traveling from  $x_{\min}$ , to  $x_{\max}$  and back to  $x_{\min}$ . Hence, the integral on the right-hand side evaluates to  $T/2$  and the normalization constant must be  $N = 2/T$ .

We're almost there! Notice that by the chain rule we have that  $dx = \left(\frac{dx}{dt}\right) dt$  and therefore  $dt = \frac{dx}{dx/dt} = dx/v(x)$  for a velocity as a function of position  $v(x)$ . The, the probability density in Equation (14.1.4) becomes

$$P(x)dx = \frac{2}{T} \frac{dx}{v(x)} \tag{14.1.5}$$

where the normalization constant  $N = 2/T$  is added.

We now go about applying the probability density in Equation (14.1.5) to the trajectory for a classical harmonic oscillator found in Equation (14.1.2). In the analysis above we went to a lot of trouble to express the

probability in terms of *position* instead of time. So, just plugging in Equation (14.1.5) to (14.1.5) would defeat that work since we'd be reintroducing time into the expression. Instead, we'll begin by rewriting the expression for the probability density in terms of energies. Note that the velocity of the oscillator is directly related to the kinetic energy which is directly related to the total energy:

$$\begin{aligned} T &= E - V(x) \\ \frac{1}{2}\mu v^2 &= E - V(x) \\ v(x) &= \sqrt{\frac{2(E - V(x))}{\mu}} \end{aligned}$$

Above,  $V(x) = \frac{1}{2}kx^2$  is the potential energy for the classical harmonic oscillator. Now, Equation (14.1.5) becomes

$$P(x)dx = \frac{2}{T} \frac{dx}{\sqrt{\frac{2(E - V(x))}{\mu}}} = \frac{2}{T} \sqrt{\frac{\mu}{2(E - V)}} dx = \frac{1}{T} \sqrt{\frac{2\mu}{E - V}} dx$$

Together, with the expression for the potential energy  $V = \frac{1}{2}kx^2$ , the relation  $k = \mu\omega^2$  defined previously, the period of oscillation  $T = 2\pi\sqrt{\frac{\mu}{k}}$ , and the total energy for a harmonic oscillator found in Equation (14.1.3), we have that

$$\begin{aligned} P(x)dx &= \frac{1}{T} \sqrt{\frac{2\mu}{E - V}} dx \\ &= \left( \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \right) \sqrt{\frac{2\mu}{\frac{1}{2}\mu b_1^2 \omega^2 - \frac{1}{2}\mu \omega^2 x^2}} dx \\ &= \frac{\omega}{2\pi} \sqrt{\frac{4}{\omega^2(b_1^2 - x^2)}} dx \\ &= \frac{1}{\pi} \frac{1}{\sqrt{b_1^2 - x^2}} dx \end{aligned} \tag{14.1.6}$$

Equation (14.1.6) represents the probability density for a classical harmonic oscillator of amplitude  $b_1$ . A plot of this probability density is illustrated in Figure 14.1.

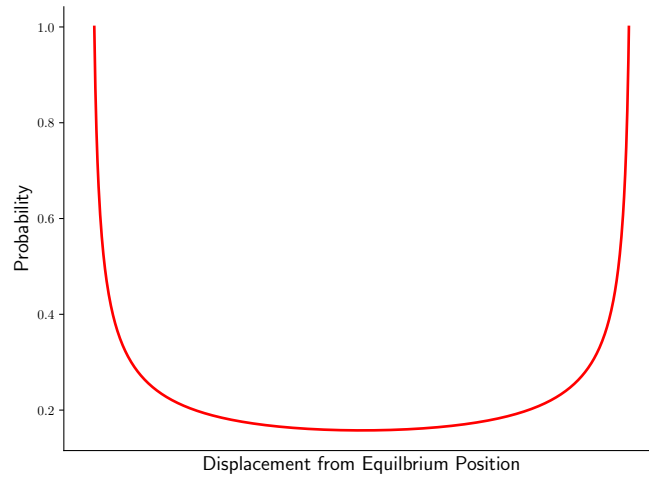


Figure 14.1: Probability density for classical harmonic oscillator. From Equation (14.1.6), the parameters are  $b_1 = 0.0008$  over an interval of  $x \in [-b_1, b_1]$ .

## 14.2 The Quantum Harmonic Oscillator

We now embark on a journey to model the *quantum mechanical* harmonic oscillator and compare our results to that of the classical model. As motivation, consider hydrogen fluoride. HF enjoys all of translational, rotational, and vibrational freedoms (for now we'll focus on exclusively vibrational freedoms), each of which contributes to the total energy of the molecule. The energy needed to stretch or compress the chemical bond, for example, can be described by some potential energy function (the Morse potential, in fact) which has a maximum and minimum, corresponding to complete overlap and an equilibrium length, respectively.

Near the equilibrium bond length and standard temperatures, the potential energy function is well approximated by that for a classical harmonic oscillator. When the distance between atoms grows much smaller than the equilibrium length, repulsive interactions between electrons in each atom dominate and the potential energy increases to infinity. At distance much larger than the equilibrium length, the overlap of electron clouds diminishes and the ability of either atom to form a chemical bond goes away. That is all to say, using the potential energy function for a classical harmonic oscillator at bond lengths far away from the equilibrium length will fail quickly.

Unlike the classical view which allows a continuous energy spectrum, the quantum mechanical view discretizes the energy spectrum. The allowed energies are determined by the Schrödinger equation. Using  $V(x) = \frac{1}{2}kx^2$  as the potential energy function as discussed in the preceding paragraph, this becomes

$$\hat{H}\psi(x) = E\psi(x) \quad (14.2.1)$$

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi(x)}{\partial x^2} + \frac{kx^2}{2} \psi(x) = E\psi(x) \quad (14.2.2)$$

where the reduced mass  $\mu$  is used for a two-body system and  $\psi(x)$  is the wave function describing the wave-particle of mass  $\mu$ .

Solving this differential equation is hard. Turning to an algebraic solution involves finding solutions in the limit that the displacement from equilibrium goes to infinity, multiply this solution by a polynomial, deriving a recursive relationship between the coefficients of said polynomial, proving that the polynomial series must terminate in order for the wave function to be normalizable, and finally deriving the eigenfunctions for  $\hat{H}$ .<sup>1</sup> Instead of putting myself through that I'll simply present the solutions to Equation (14.2.1):

$$\psi_n(x) = A_n \mathcal{H}_n(\alpha^{1/2}x) e^{-\alpha x^2/2} \quad (14.2.3)$$

Here,

$$A_n = \frac{1}{\sqrt{2^n n!}} \left( \frac{\alpha}{\pi} \right)^{1/4} \quad (14.2.4)$$

is the normalization constant of the wave function,

$$\mathcal{H}_n(u) = (-1)^n e^{u^2} \frac{d^n}{du^n} \left( e^{-u^2} \right) \quad (14.2.5)$$

is the  $n$ th *Hermite polynomial*, and  $\alpha = \sqrt{\mu k / \hbar^2} = \mu \omega / \hbar$  is a constant. In the expression above we can see that if  $n$  is an even number,  $\mathcal{H}_n$  is an even (symmetric) function, and if  $n$  is odd,  $\mathcal{H}_n$  is an odd function. This symmetry will be helpful when we consider the orthogonality of wave functions for the quantum mechanical

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<sup>1</sup>If you're interested in this derivation it can be found here: [https://ocw.mit.edu/courses/physics/8-04-quantum-physics-i-spring-2013/lecture-notes/MIT8\\_04S13\\_Lec08.pdf](https://ocw.mit.edu/courses/physics/8-04-quantum-physics-i-spring-2013/lecture-notes/MIT8_04S13_Lec08.pdf)

harmonic oscillator. The first few eigenfunctions of Equation (14.2.3) are listed below:

$$\begin{aligned}\psi_0(x) &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \\ \psi_1(x) &= \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} \\ \psi_2(x) &= \left(\frac{\alpha}{4\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2} \\ \psi_3(x) &= \left(\frac{\alpha^3}{9\pi}\right)^{1/4} (2\alpha x^3 - 3x) e^{-\alpha x^2/2} \\ &\vdots\end{aligned}$$

Note that all of the Hermite polynomials are either even or odd functions and that each is orthogonal to one another. Moreover, they form a complete set for all possible eigenfunctions of the Schrödinger equation.

For any wave function listed above, a necessary boundary condition is that the amplitude must remain finite for large displacements from the equilibrium position. This condition gives rise to quantization for the quantum mechanical harmonic oscillator. The energy eigenvalues are

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) = h\nu \left(n + \frac{1}{2}\right), \quad n = 1, 2, 3, \dots \quad (14.2.6)$$

A more detailed solution to the wave functions and allowed energies for the quantum mechanical oscillator can be found in Appendix ???. An important aspect of the energies to keep in mind is that *the energy eigenvalues are evenly spaced at a distance of  $h\nu$  from one another*. This is in contrast to the particle in a box which had energy level spacings grow quadratically.

Once again, we've seen how boundary conditions and confinement lead to quantization of energy and a discrete energy spectrum. Similar to the particle in a box, the quantum mechanical harmonic oscillator has a nonzero zero-point energy. This condition can be thought of as being brought about due to the confinement caused by attaching the quantum particle to a spring, thereby limiting its motion. As the spring is made more stiff ( $k$  increases and therefore the vibrational frequency increases), the particle is constrained to a greater extent and the zero-point energy increases in magnitude. An identical trend is observed for a particle in a box when the length of the box is shortened.

Lastly, I'll note that the quantum mechanical harmonic oscillator and classical harmonic oscillator have the same frequency of vibration:

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (14.2.7)$$

### 14.2.1 Probability Density for a Quantum Harmonic Oscillator

As was done for the classical harmonic oscillator we'll now look at the probability density for the quantum harmonic oscillator. Unlike before, however, finding the probability density will differ by the postulates of quantum mechanics; in this case, we are interested simply in the quantity  $\psi_n^*(x)\psi_n(x)dx$  which represents the probability.

In Figure 14.2 we see that the wave functions and probability densities somewhat resemble those of a particle trapped in a box. The grey area represents the classically forbidden region. Unlike the classical harmonic oscillator which is never displaced beyond its turning points, the quantum harmonic oscillator tunnels beyond this barrier into the forbidden region.

An interesting comparison that can be made is the convergence of the probability density of the quantum mechanical oscillator to that of the classical oscillator, in Figure 14.3. As the energy level of the quantum

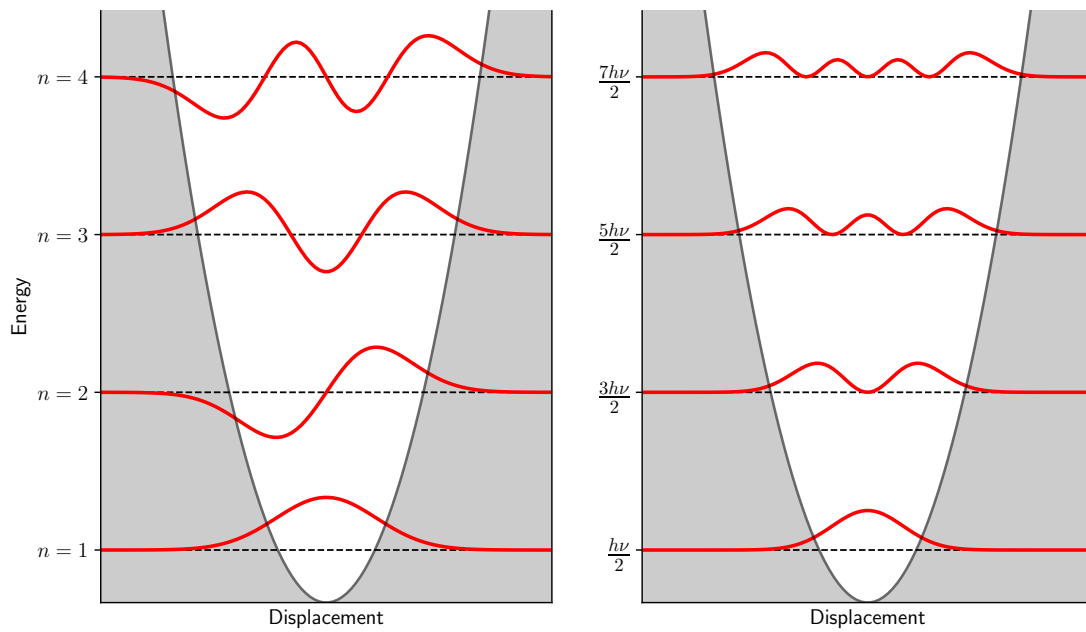


Figure 14.2: (Left) The wave functions for the first four energy levels of the quantum mechanical harmonic oscillator. (Right) The probability densities for the first four energy levels of the quantum mechanical harmonic oscillator. In both plots, the grey area represents the classically forbidden region. Similar to the particle in a box, quantum particles are allowed to tunnel through the classical turning point with a small probability, as depicted in the graph.

oscillator increases, the probability density looks more and more like that of the classical oscillator. Intuitively, this makes sense because of the correspondence principle.

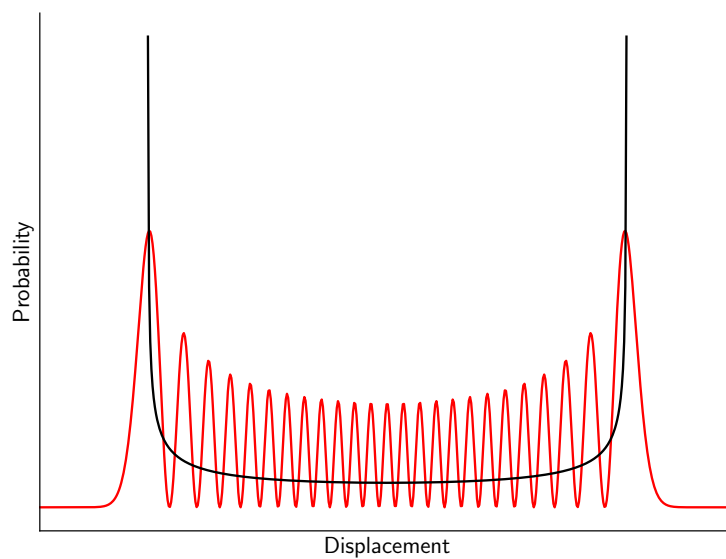


Figure 14.3: In red is the probability density for the  $n = 24$  energy level of a quantum mechanical harmonic oscillator. In black is the probability density for a classical harmonic oscillator

### 14.3 Rotational Motion

So far we've considered quantum mechanical models which deal with *translational motion* which are easily expressed using the cartesian coordinates  $x$ ,  $y$ , and  $z$ . In these systems, the velocity, momentum, and acceleration vectors are all parallel to the directions of motion and the equations of motion (i.e., the Schrödinger equation) is easily written. *Rotational motion*, however, does not enjoy these properties and requires alternative definitions for the corresponding *angular* vectors, such as angular velocity, angular momentum, and centripetal acceleration.

The *rigid rotor* is a simple example of angular motion; it is a good model for thinking about rotational motion of a diatomic molecule and relies on the assumption that there is no stretching of the bond, hence *rigid*. In the rotating systems under consideration, there are no forces which oppose the angular motion and therefore no potential energy can be stored in the system. In the absence of dissipative forces such as friction or an external potential energy field, all energy stored in the rigid rotor is kinetic and retained indefinitely.

We first define the *centripetal acceleration* as

$$a = \frac{|\vec{v}|^2}{r} \quad (14.3.1)$$

for some velocity vector  $\vec{v}$  and radius  $r$ . Note that this definition extends to  $n$ -dimensions. In circular motion, the analog to displacement is *angle*, that is, the total angle passed through after some time. Hence, the angular velocity  $\omega$  is defined as

$$|\vec{\omega}| = \frac{d\theta}{dt} \quad (14.3.2)$$

and the angular acceleration  $\alpha$  is

$$\alpha = \frac{d^2\theta}{dt^2} \quad (14.3.3)$$

The decision to use  $\omega$  to represent both angular velocity and frequency is sort of unfortunate, so hopefully context clues will be enough to allow us to distinguish which is being represented at any given time. The directions of the vectors  $\vec{\omega}$  and  $\vec{\alpha}$  point along the axis of rotation and are determined by the right hand rule. By the definition of the angular velocity we're also left with the relation  $\vec{v} = r\vec{\omega}$  for a radius  $r$ .

The definitions above are enough to quantify the common forms of energy we deal with most often. The kinetic energy becomes

$$T_{\text{rot}} = \frac{1}{2}\mu v^2 = \frac{1}{2}\mu(r\omega)^2 = \frac{1}{2}\mu r^2\omega^2 = \frac{1}{2}I\omega^2 \quad (14.3.4)$$

for a reduced mass  $\mu$ . Here, we introduce a new quantity  $I = \mu r^2$ , the *moment of inertia*, which measures the rotational inertia of an object, i.e., the extent to which an object opposes a torque. With the moment of inertia, the kinetic energy takes a more recognizable form with  $I$  taking the place of  $\mu$  and  $\omega$  taking the place of  $v$ .

Lastly, we'll develop a relationship similar to Newton's second law,  $F = m\vec{a} = \frac{d\vec{p}}{dt}$ , for angular motion. We start by defining the angular momentum  $\vec{L}$  as

$$\vec{L} = \vec{r} \times \vec{p} = (yp_z - zp_y)\hat{i} + (zp_x - xp_z)\hat{j} + (xp_y - yp_x)\hat{k} \quad (14.3.5)$$

for a radial vector  $\vec{r} = (x, y, z)$  and momentum vector  $\vec{p} = (p_x, p_y, p_z)$ . The  $\times$  symbol represents a *cross product* and the vectors  $\hat{i}$ ,  $\hat{j}$ , and  $\hat{k}$  the unit vectors in each of the  $x$ ,  $y$ , and  $z$  coordinate directions. The magnitude of the angular momentum is given by

$$|\vec{L}| = |\vec{r} \times \vec{p}| = rp \sin \phi = r\mu v \sin \varphi \quad (14.3.6)$$

where  $|\vec{r}| = r$  and  $|\vec{p}| = p$ . Also, the substitution  $p = \mu v$  was taken directly from the definition of the linear momentum. Note that  $\varphi$  is the angle between the vector  $\vec{r}$  and  $\vec{p}$ ; though, in angular motion  $\vec{r}$  and  $\vec{p}$  are always perpendicular so that  $\varphi = \pi/2$  and  $|\vec{L}| = r\mu v$ . So, we can express the kinetic energy as

$$T_{\text{rot}} = \frac{p^2}{2\mu} = \frac{|\vec{L}|^2}{\mu r^2} = \frac{|\vec{L}|^2}{2I} \quad (14.3.7)$$

Classical physics predicts that an object undergoing rotational motion can take on any angular momentum  $\vec{L}$  and therefore any kinetic energy, by Equation (14.3.7). From the Stern-Gerlach experiment, however, we know that the angular momentum of quantum particles is quantized and therefore  $L$  takes on only particular values. Hence, the kinetic energy of a particular undergoing rotational motion must *also* take on only particular values and is the reason we (will) see a discrete energy spectrum for the quantum mechanical rigid rotor. Also, this agrees with our intuition about quantum particles having a quantized set of energies no matter the *type* of energy.

## 14.4 Quantum Mechanical Rotation

To a fair approximation, the three types of motion—rotational, translational, and vibrational—can be dealt with independently. Although these types of motion are not completely decoupled (consider how a spring might stretch when rotated quickly enough; In this way, rotation and vibration are coupled), the approximation is rather exact. Neglecting coupling, the total energy for any particle can be written

$$E = E_{\text{trans}}(\rho) + E_{\text{rot}}(\theta, \varphi) + E_{\text{vib}}(\tau) \quad (14.4.1)$$

where  $\rho$ ,  $\theta$ , and  $\varphi$  refer to the spatial coordinates *of the center of mass* in spherical coordinates, and  $\tau$  refers to the vibrational amplitude of the molecule. Since these energies can be written as functions of independent variables, we can write the Hamiltonian as

$$\hat{H} = \hat{H}_{\text{trans}}(\rho) + \hat{H}_{\text{rot}}(\theta, \varphi) + \hat{H}_{\text{vib}}(\tau) \quad (14.4.2)$$

and the wave function for the particle can be expressed as a product of the wave functions representing each motion:

$$\Psi_n(\rho, \theta, \varphi, \tau) = R(\rho)Y(\theta, \varphi)\Lambda(\tau) \quad (14.4.3)$$

where  $R(\rho)$  represents the spatial/translational contribution to  $\Psi$ ,  $Y(\theta, \varphi)$  the rotational contribution, and  $\Lambda(\tau)$  is the vibrational contribution. Going forward, in two-dimensions we'll make the simplification  $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$  to make it clear the contributions in two- versus three-dimensions. Because we're able to express the wave function as a product of independent terms, the Schrödinger equation for the wave function may be solved by separation of variables.

### 14.4.1 Quantum Mechanical Rotation in 2 Dimensions

For now, we will limit our discussion to the rigid rotor in two-dimensions such that a particle under consideration experiences no vibrational freedom and the length of the bond between atoms does not change. That is,  $\rho$  remains constant and the vibrational contribution to the total energy is zero. In this case, the Schrödinger

equation may be written<sup>2</sup>

$$\begin{aligned}
 \hat{H}\Psi &= -\frac{\hbar^2}{2\mu}\nabla^2\Psi_n = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2}\right)_{\rho=\rho_0} \\
 &= -\frac{\hbar^2}{2\mu}\left(\frac{1}{\rho}\frac{\partial}{\partial\rho}\left[\rho\frac{\partial R(\rho)}{\partial\rho}\right] + \frac{1}{\rho^2}\frac{\partial^2\Theta(\theta)}{\partial\theta^2}\right)_{\rho=\rho_0} \\
 &= -\frac{\hbar^2}{2\mu\rho_0^2}\frac{\partial^2\Theta(\theta)}{\partial\theta^2} = E\Theta(\theta)
 \end{aligned} \tag{14.4.4}$$

Equation (14.4.4) has the same functional form as the Schrödinger equation for a free particle in cartesian coordinates, as we've seen previously. Solutions to this equation are

$$\Theta_1(\theta) = c_1 e^{ik\theta} \quad \& \quad \Theta_2(\theta) = c_2 e^{-ik\theta} \tag{14.4.5}$$

for some constants  $c_1$ ,  $c_2$ , and  $k$ , each of which is dependent on the initial conditions of the system. Upon properly normalizing these wave functions we find that  $c_1 = c_2 = 1/\sqrt{2\pi}$ .

To obtain physically meaningful solutions to Equation (14.4.4) we require boundary conditions on the wave function. Just as we've restricted particles by putting them in a box or attaching them to a spring, we'll restrict the motion of this particle by requiring *periodicity*, that is, the condition that there is no way to distinguish between a particle that has rotated  $n$  times around the circle versus  $n + 1$  times around the circle. In other words, for a given angle of rotation  $\theta$ , the particle should be characterized identically at  $\theta$  and  $\theta + 2\pi$ . Using  $\Theta_1$  as an example, we require

$$\begin{aligned}
 \Theta_1(\theta) &= \Theta_1(\theta + 2\pi) \Rightarrow c_1 e^{ik\theta} = c_1 e^{ik(\theta + 2\pi)} \\
 &\Rightarrow e^{i(2\pi k)} = 1 \\
 \cos(2\pi k) + i \sin(2\pi k) &= 1
 \end{aligned}$$

by Euler's formula. This condition is satisfied if and only if  $k = 0, \pm 1, \pm 2, \pm 3, \dots$  and therefore generates the quantization rules for the constant  $k$ . This quantum number is also oftentimes written  $m_l$  and is related to the angular momentum vector. The choice of  $m_l$  to represent this quantum number will become more clear when we consider quantum mechanical rotation in three dimensions.

For now, however, we'll consider how the wave function  $\Theta_1$  behaves under certain operators. One of the most ubiquitous and important properties of quantum mechanical particles is the angular momentum. From Equation (14.3.5) we can express the angular momentum operator as

$$\begin{aligned}
 \hat{L} &= \left(-i\hbar y \frac{\partial}{\partial z} + i\hbar z \frac{\partial}{\partial y}\right)\hat{i} + \left(-i\hbar z \frac{\partial}{\partial x} + i\hbar x \frac{\partial}{\partial z}\right)\hat{j} + \left(-i\hbar x \frac{\partial}{\partial y} + i\hbar y \frac{\partial}{\partial x}\right)\hat{k} \\
 &= \hat{L}_x + \hat{L}_y + \hat{L}_z
 \end{aligned}$$

with  $\hat{L}_u$  representing the angular momentum in the  $u$  direction. Soon we'll be interested in using these operators in different coordinate systems such as polar and spherical. Briefly, I'll note that the  $z$ -component of the momentum operator may be expressed as

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\theta} \tag{14.4.6}$$

The other angular momentum operators are unwieldy and unfriendly. Luckily, for the most part we'll only ever be interested in the angular momentum in the  $z$  direction. Moreover, we can always just shift the coordinate system such that the angular momentum we're interested in orients in the  $z$  direction, if need be.

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<sup>2</sup>Appendix ?? contains discussion on the Laplacian operator in different coordinate systems.



Using  $\hat{L}_z$ , we can operate on either of the wave functions in (14.4.5), after proper normalization:

$$\hat{L}_z \Theta_1 = -i\hbar \frac{\partial}{\partial \theta} \left[ \frac{e^{im_l \theta}}{\sqrt{2\pi}} \right] = m_l \hbar \frac{e^{im_l \theta}}{\sqrt{2\pi}} = m_l \hbar \Theta_1 \quad (14.4.7)$$

Thus, the angular momentum for the quantum mechanical two dimensional rotor is quantized such that  $L_z = \pm m_l \hbar$ , depending on the quantum number  $m_l$ .

Using the quantum numbers  $m_l = 0, \pm 1, \pm 2, \pm 3, \dots$  in Equation (14.4.4) allows us to determine the energies for the quantum mechanical rigid rotor in two dimensions. We'll use  $\Theta_1(\theta)$  as an example:

$$\begin{aligned} -\frac{\hbar^2}{2\mu\rho_0^2} \frac{\partial^2 \Theta_1(\theta)}{\partial \theta^2} &= -\frac{\hbar^2}{2\mu\rho_0^2} \frac{\partial^2}{\partial \theta^2} [c_1 e^{im_l \theta}] \\ &= -\frac{\hbar^2}{2\mu\rho_0^2} (-c_1 m_l^2 e^{im_l \theta}) \\ &= \frac{\hbar^2 m_l^2}{2\mu\rho_0^2} \Theta_1 = E \Theta_1 \end{aligned}$$

Thus, the discretized set of energies is given by

$$E_{m_l} = \frac{\hbar^2 m_l^2}{2\mu\rho_0^2} = \frac{\hbar^2 m_l^2}{2I} \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad (14.4.8)$$

Importantly, note that the energy levels corresponding to  $m_l$  and  $-m_l$  have the same energies while the wave functions describing these states are orthogonal. This implies that the energy levels  $E_{m_l}$  and  $E_{-m_l}$  are *degenerate*.

Recall that earlier we determined that the kinetic energy of a rigid rotor in the absence of any external forces is given by Equation (14.3.4); this equivalence must also hold for a quantum mechanical rigid rotor. Thus, in conjunction with Equation (14.4.8) which we've just derived, we're left with the relationship

$$\begin{aligned} \frac{\hbar^2 m_l^2}{2I} &= \frac{1}{2} I \omega^2 \\ \omega^2 &= \frac{\hbar^2 m_l^2}{I^2} \\ \omega &= \frac{\hbar m_l}{I} \end{aligned} \quad (14.4.9)$$

which is the quantization of angular velocity for the quantum mechanical rigid rotor.

A final point I'll make about the rigid rotor is that unlike the particle in a box or the quantum mechanical harmonic oscillator, there is no zero-point energy associated with the quantum rigid rotor in two dimensions. When  $m_l = 0$ , the  $E_{m_l} = 0$ . This is because a zero-point energy appears only if a region of potential energy confines the motion of a quantum particle to a limited region. Clearly, this is not the case for a rotor because our boundary condition was periodicity and not a region in space. In any real fluid which experiences all degrees of rotational, translational, and vibrational freedoms, the zero-point energy arises from the translational and vibrational motions.

### 14.4.2 Quantum Mechanical Rotation in 3 Dimensions

To introduce nothing but complication and difficulty, we now consider the rigid rotor in three dimensions. Similar to the case of two dimensions, the radius of rotation stays constant such that  $\rho = \rho_0$ . In contrast to two dimensions, however, zenith angle  $\varphi$  is no longer zero and is instead allowed to vary in space. This introduces a second degree of freedom into the system, along with the freedom of the azimuthal angle  $\theta$  already.

We'll begin by writing the Schrödinger equation in spherical coordinates just as before. Suppose that the wave function for this three dimensional rigid rotor can be written such that  $\Psi(\rho, \theta, \varphi) = R(\rho)Y(\theta, \varphi)$  where  $\theta$

and  $\varphi$  are no longer decoupled. In the absence of any external forces (e.g., an external potential energy),

$$\begin{aligned}\hat{H}\Psi &= -\frac{\hbar^2}{2\mu}\nabla^2\Psi_n = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right)_{\rho=\rho_0} \\ &= -\frac{\hbar^2}{2\mu}\left[\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R(\rho)}{\partial\rho}\right) + \frac{1}{\rho^2\sin^2\varphi}\frac{\partial^2 Y(\theta,\varphi)}{\partial\theta^2} + \frac{1}{\rho^2\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial Y(\theta,\varphi)}{\partial\varphi}\right)\right]_{\rho=\rho_0} \\ &= -\frac{\hbar^2}{2\mu\rho_0^2}\left[\frac{1}{\sin^2\varphi}\frac{\partial^2 Y(\theta,\varphi)}{\partial\theta^2} + \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial Y(\theta,\varphi)}{\partial\varphi}\right)\right] = EY(\theta,\varphi)\end{aligned}$$

Following a little bit of algebraic gymnastics and the substitution  $I = \mu\rho_0^2$ , we can rearrange this equation to afford

$$\left[\frac{1}{\sin^2\varphi}\frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\varphi}\right)\right]Y(\theta,\varphi) = -\frac{2IE}{\hbar^2}Y(\theta,\varphi) \quad (14.4.10)$$

Since this problem is a differential equation in two variables, our first plan of attack should be to try and write (14.4.10) as a separable equation, such that  $\theta$  and  $\varphi$  appear separately. Recall that this is possible only if the Hamiltonian can be written  $\hat{H} = \hat{H}_\theta + \hat{H}_\varphi$ . Though, it's not immediately clear how we might go about this... Nevertheless, we'll postulate that the equation is separable and assert that  $Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$  and make this substitution into Equation (14.4.10):

$$\begin{aligned}\left[\frac{1}{\sin^2\varphi}\frac{\partial^2}{\partial\theta^2} + \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial}{\partial\varphi}\right)\right]\Theta(\theta)\Phi(\varphi) &= -\frac{2IE}{\hbar^2}\Theta(\theta)\Phi(\varphi) \\ \frac{\Phi}{\sin^2\varphi}\frac{\partial^2\Theta}{\partial\theta^2} + \frac{\Theta}{\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\Phi}{\partial\varphi}\right) &= \end{aligned} \quad (14.4.11)$$

Dividing both side through by  $\Theta(\theta)\Phi(\varphi)$  affords

$$\frac{1}{\Theta\sin^2\varphi}\frac{\partial^2\Theta}{\partial\theta^2} + \frac{1}{\Phi\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\Phi}{\partial\varphi}\right) = -\frac{2IE}{\hbar^2} \quad (14.4.12)$$

and multiplying through by  $\sin^2\varphi$  separates the variables:

$$\frac{1}{\Theta}\frac{\partial^2\Theta}{\partial\theta^2} + \frac{\sin\varphi}{\Phi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\Phi}{\partial\varphi}\right) = -\frac{2IE}{\hbar^2}\sin^2\varphi \quad (14.4.13)$$

In this process we've introduced  $\varphi$  dependence on the right-hand side of the Schrödinger equation. Although this isn't optimal, we can still consider the nature of solutions *at a constant*  $\varphi$  and sample solutions to  $\Theta$ . Then, Equation (14.4.13) takes the form

$$\frac{1}{\Theta}\frac{\partial^2\Theta}{\partial\theta^2} + a_1 = a_2$$

for some constants  $a_1$  and  $a_2$ . Combining constants and rearranging affords

$$\frac{\partial^2\Theta}{\partial\theta^2} = -m_l^2\Theta$$

for some new constant  $m$ . The solutions to this equation are exactly those which we saw for the two dimensional rigid rotor. Namely,

$$\Theta_1(\theta) = \frac{1}{\sqrt{2\pi}}e^{im_l\theta} \quad \& \quad \Theta_2(\theta) = \frac{1}{\sqrt{2\pi}}e^{-im_l\theta} \quad m_l = 0, 1, 2, 3 \dots \quad (14.4.14)$$

after proper normalization. Here  $m_l$  is restricted to integer values because we require a single-valued wave function.

An alternative approach to determining the functional forms of  $\Theta(\theta)$  and  $\Phi(\varphi)$  is to rewrite Equation

(14.4.13) as

$$\frac{\sin \varphi}{\Phi} \frac{\partial}{\partial \varphi} \left( \sin \varphi \frac{\partial \Phi}{\partial \varphi} \right) + \frac{2IE}{\hbar^2} \sin^2 \varphi = -\frac{1}{\Theta} \frac{\partial^2 \Theta}{\partial \theta^2}$$

Now, both sides vary with respect to different variables. However, the equivalence must hold for all physically plausible solutions to the wave function so that both sides must be equal to some constant:

$$\frac{\sin \varphi}{\Phi} \frac{\partial}{\partial \varphi} \left( \sin \varphi \frac{\partial \Phi}{\partial \varphi} \right) + \frac{2IE}{\hbar^2} \sin^2 \varphi = m_l^2 \quad (14.4.15)$$

$$-\frac{1}{\Theta} \frac{\partial^2 \Theta}{\partial \theta^2} = m_l^2 \quad (14.4.16)$$

Clearly this affords the same solution to  $\Theta(\theta)$  as before. Equation (14.4.15), meanwhile, may be solved but is more difficult and beyond the scope of what I care about at this time. The necessary conditions for Equation (14.4.15) to satisfy the Schrödinger equation are

$$\frac{2IE}{\hbar^2} = l(l+1), \quad l = 0, 1, 2, 3, \dots$$

$$m_l = -l, -(l-1), -(l-2), \dots, 0, \dots, (l-2), (l-1), l$$

where both  $l$  and  $m_l$  are integers. The quantum number  $m_l$  we've been introduced to before;  $l$  is another quantum number. For a given value of  $l$ , there are  $2l+1$  unique values of  $m_l$ .

The logical question to ask yourself at this point is, why do two quantum numbers occur for rotation in three dimensions? The answer lies in how the rigid rotor has two degrees of freedom, both  $\theta$  and  $\varphi$ , as mentioned earlier. Hence, two quantum numbers appear. This is the same reason that only one quantum number  $n$  is required to characterize the particle in a one dimensional box whereas  $n_x$ ,  $n_y$ , and  $n_z$  are all necessary to completely characterize a particle confined to a three dimensional box.

To stress the importance of both quantum numbers  $l$  and  $m_l$ , the function  $Y(\theta, \varphi)$  is often written

$$Y(\theta, \varphi) = Y_l^{m_l}(\theta, \varphi) = \Theta_{m_l}(\theta) \Phi_l^{m_l}(\varphi) \quad (14.4.17)$$

where  $\Theta_{m_l}$  is dependent on only a single quantum number where  $\Phi_l^{m_l}$  relies on both  $l$  and  $m_l$ .

From the restrictions placed on  $l$  and  $m_l$  we see that the energy of the rigid rotor in three dimensions must be given by

$$E_l = \frac{\hbar^2}{2I} l(l+1), \quad l = 0, 1, 2, 3, \dots \quad (14.4.18)$$

An interesting comparison made between the total energy of the two-dimensional and three-dimensional rigid rotors is their dependence on quantum numbers. In the case of two dimensions, Equation (14.4.8) illustrates that the total energy relies on only  $m_l$ . In contrast, above we see that in three dimensions the total energy relies only on  $l$ . As discussed briefly earlier, the quantum number  $m_l$  is related to the angular momentum of a quantum particle *in the  $z$  direction*. Also, recall from Equation (14.3.7) that the total energy (in the absence of an external potential energy) is dependent on the *magnitude of the angular momentum* and is ignorant to direction. Therefore, all  $2l+1$  quantum numbers  $m_l$  which have the same value of  $l$  have the same total energy eigenfunctions yet different values of  $m_l$ . Thus, since each wave function with a different  $m_l$  is orthogonal to one another, those with the same  $l$  and different  $m_l$  are *degenerate eigenfunctions of the total energy operator*.

In the case of two dimensions,  $m_l$  represents the *only* angular momentum vector and therefore characterizes the total energy of the system.<sup>3</sup> This is in contrast to three dimensions where there are three simultaneous angular momentum vectors in each of the three coordinate directions. Hence, the magnitude of the total angular

<sup>3</sup>This goes back to what I mentioned earlier in that no matter what the orientation of our rigid rotor is we can always align the coordinate axes such that the direction of the angular momentum is in the  $z$  direction. The important takeaway for this point, though, is that in two dimensions there is a single angular momentum vector, point out of the plane of rotation.

momentum (which encapsulates the angular momentum in all three directions) is necessary to capture the total energy of the rigid rotor in three dimensions.

### 14.4.3 The Spherical Harmonics

*Spherical harmonic functions* are special functions defined on the surface of a sphere; they form a complete set of orthogonal functions and thus an orthonormal basis. The spherical harmonics themselves originate from solve Laplace's equation,  $\nabla^2 f = 0$  for some scalar field  $f$ , in spherical coordinates, hence the name. If we take the scalar field of interest to be a wave function  $\Psi$ , Laplace's equation becomes

$$\begin{aligned}\nabla^2 \Psi &= \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \\ &= \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial \Psi}{\partial \rho} \right) + \frac{1}{\rho^2 \sin^2 \varphi} \frac{\partial^2 \Psi}{\partial \theta^2} + \frac{1}{\rho^2 \sin \varphi} \frac{\partial}{\partial \varphi} \left( \sin \varphi \frac{\partial \Psi}{\partial \varphi} \right)\end{aligned}$$

which is exactly the functional form of the Schrödinger equation for the quantum mechanical rigid rotor, up to a constant.

If we write the wave function for the three-dimensional quantum mechanical rotor as  $\Psi = R(\rho)Y(\theta, \varphi)$ , as we saw in the previous section, the angular component of the wave function may be written as  $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$  and each of  $\Theta$  and  $\Phi$  may be solved. The solution to  $\Theta$  is presented in Equation (14.4.14). The solutions to  $\Phi$  may also be determined, although finding an expression involves a lot more math than is necessary. So, some solutions to  $Y_l^{m_l}(\theta, \varphi)$  are presented below without justification:

$$\begin{aligned}Y_0^0(\theta, \varphi) &= \left( \frac{1}{4\pi} \right)^{1/2} \\ Y_1^0(\theta, \varphi) &= \left( \frac{3}{4\pi} \right)^{1/2} \cos \varphi \\ Y_1^{\pm 1}(\theta, \varphi) &= \left( \frac{3}{8\pi} \right)^{1/2} e^{\pm i\theta} \sin \varphi \\ Y_2^0(\theta, \varphi) &= \left( \frac{5}{16\pi} \right)^{1/2} e^{\pm i\theta} (3 \cos^2 \varphi - 1) \\ Y_2^{\pm 1}(\theta, \varphi) &= \left( \frac{15}{8\pi} \right)^{1/2} e^{\pm i\theta} \sin \varphi \cos \varphi \\ Y_2^{\pm 2}(\theta, \varphi) &= \left( \frac{15}{32\pi} \right)^{1/2} e^{\pm 2i\theta} \sin^2 \varphi\end{aligned}$$

As we saw earlier in the solutions to  $\Theta_l(\theta)$ , the solutions to this function are periodic. The  $\varphi$  dependence enters as a polynomial in sine and cosine. The constant factor in front of each expression is a normalizing constant. For instance,  $Y_0^0(\theta, \varphi)$  has a normalizing constant of  $1/\sqrt{4\pi}$ . So, we can deduce that the integral of  $(Y_0^0)^2 d\theta d\varphi$  over all  $\theta$  and  $\varphi$  without normalization goes to  $4\pi$  which is exactly the surface area of the unit sphere. In other words,  $Y_0^0$  corresponds to an  $s$  orbital.

Notice that unless  $m_l = 0$ , the spherical harmonics are complex functions. So, it is customary to instead form linear combinations of  $Y_l^{m_l}$  to generate real functions which can be plotted and visualized. The following are descriptions of the  $p$  and  $d$  orbitals for hydrogen, illustrated as linear combinations of the spherical harmonics

and as functions of  $\theta$  and  $\varphi$ .

$$\begin{aligned} p_x &= \frac{Y_1^1 + Y_1^{-1}}{\sqrt{2}} = \left(\frac{3}{4\pi}\right)^{1/2} \sin \varphi \cos \theta \\ p_y &= \frac{Y_1^1 - Y_1^{-1}}{i\sqrt{2}} = \left(\frac{3}{4\pi}\right)^{1/2} \sin \varphi \sin \theta \\ p_z &= Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta \end{aligned}$$

The wave functions for the  $p$  orbitals form a set of mutually orthogonal dumbbells, each of which has the same amplitude but a different sign (positive or negative) for the two lobes. Also, each wave function has a nodal plane corresponding to the plane which is normal to the axis aligned with the dumbbell. Intuitively, the presence of this plane should make sense when we think of the orbitals in the context of angular momentum, as we've been doing. We can always deduce the  $z$  component of the angular momentum, as we've already discussed, and if the angular momentum vector lied in any one of the coordinate planes we would be able to deduce an exact value for another component of the vector. Then, we would know two components of the angular momentum vector which is in direct violation of the uncertainty principle.

$$\begin{aligned} d_{z^2} &= Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \varphi - 1) \\ d_{xz} &= \frac{Y_2^1 + Y_2^{-1}}{\sqrt{2}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin \varphi \cos \varphi \cos \theta \\ d_{yz} &= \frac{Y_2^1 - Y_2^{-1}}{i\sqrt{2}} = \left(\frac{15}{4\pi}\right)^{1/2} \sin \varphi \cos \varphi \sin \theta \\ d_{x^2-y^2} &= \frac{Y_2^2 + Y_2^{-2}}{\sqrt{2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \varphi \cos 2\theta \\ d_{xy} &= \frac{Y_2^2 - Y_2^{-2}}{i\sqrt{2}} = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \varphi \sin 2\theta \end{aligned}$$

The  $d$  orbitals have more complex wave functions and therefore more complex three-dimensional shapes. In contrast to the  $p$  orbitals, there are two nodal planes separating these lobes in four of the five  $d$  orbitals, the exception being the orbital which is aligned with the  $z$  axis ( $d_{z^2}$ ). The introduction of more nodal planes arises because  $l$  is larger for the  $d$  orbitals than for the  $p$  orbitals. This is similar to the particle in a box model where increasing the quantum number  $n$  introduced more nodes to the wave function of the particle.

## 14.5 Quantization of Angular Momentum

Here we continue the discussion on the quantum mechanical rigid rotor in three dimensions, this time in the context of *angular momentum* rather than energy. As we've seen time and time again, angular momentum is incredibly important in quantum chemistry. For example, the  $s$ ,  $p$ , and  $d$  electrons depend on the quantum numbers  $l$  and  $m_l$ , which we've seen are directly related to the angular momentum.

As we saw earlier in Equation (14.4.7), the wave function for a two dimensional rigid rotor is an eigenfunction of the angular momentum operator  $\hat{L}_z$ . It is not difficult to show that the wave function for the three dimensional rigid rotor enjoys the same properties. Because the potential energy of a free rotor is zero, the total energy stored in the rotor is given by Equation (14.3.7), written

$$E = \frac{|\vec{l}|^2}{2I}$$

for an angular momentum vector  $\vec{l}$  and moment of inertia  $I$ . Since  $E$  and  $|\vec{l}|^2$  differ by only a constant,  $1/2I$ ,

the corresponding operators  $\hat{H}$  and  $\hat{l}^2$ , differ by only a constant as well. Thus,  $\hat{H}$  and  $\hat{l}^2$  share a common set of eigenfunctions and therefore commute, i.e., we can know both the total energy and angular momentum of a particle simultaneously and exactly.

Recall from Equation (14.4.18) that the total energy of the quantum mechanical rigid rotor in three dimensions is  $E = \frac{\hbar^2}{2I}l(l+1)$  which implies that  $\hat{H}Y_l^{m_l} = \frac{\hbar^2}{2I}l(l+1)Y_l^{m_l}$ . Using the proportionality mentioned a moment ago, we can immediately write,

$$\hat{l}^2 Y_l^{m_l}(\theta, \varphi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta, \varphi) \quad (14.5.1)$$

illustrating that the quantum numbers  $l$  and  $m_l$  are defining indices for the eigenfunctions of  $\hat{H}$  and  $\hat{l}^2$ . That is,  $l$  and  $m_l$  explicitly determine the functional form and energy of the wave function.

Since the eigenvalues of  $\hat{l}^2$  are  $\hbar^2 l(l+1)$ , the only observable quantities for  $|\vec{l}|^2$  are  $\hbar^2 l(l+1)$  and therefore the magnitude of the angular momentum is quantized such that  $|\vec{l}| = \hbar\sqrt{l(l+1)}$ .

Importantly, note that the operators  $\hat{l}^2$  and  $\hat{H}$  commute, *not*  $\hat{l}$  and  $\hat{H}$ . Considering the operator  $\hat{l}$  in three dimensions, it may be written  $\hat{l} = (\hat{l}_x, \hat{l}_y, \hat{l}_z)$ . The functional form of these operators are listed above for cartesian coordinates. The corresponding operators in spherical coordinates are

$$\hat{l}_x = -i\hbar \left( -\sin\theta \frac{\partial}{\partial\varphi} - \cot\varphi \cos\theta \frac{\partial}{\partial\theta} \right) \quad (14.5.2)$$

$$\hat{l}_y = -i\hbar \left( \cos\theta \frac{\partial}{\partial\varphi} - \cot\varphi \sin\theta \frac{\partial}{\partial\theta} \right) \quad (14.5.3)$$

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial\theta} \quad (14.5.4)$$

Also, the commutators between each of these three operators are cyclic:

$$[\hat{l}_x, \hat{l}_y] = i\hbar\hat{l}_z$$

$$[\hat{l}_y, \hat{l}_z] = i\hbar\hat{l}_x$$

$$[\hat{l}_z, \hat{l}_x] = i\hbar\hat{l}_y$$

Thus, we can never know more than one of the components of the angular momentum vector simultaneously and exactly. So, the direction of the angular momentum vector can never be known exactly. Considering Equation (14.5.4), however, we find that the angular momentum in the  $z$  direction may be computed with relative ease since it depends only on the variable  $\theta$ . Performing this operation on the wave function  $Y_l^{m_l}(\theta, \varphi) = \Theta_{m_l}(\theta)\Phi_l^{m_l}(\varphi)$  and using the result for  $\Theta$  from Equation (14.4.14), we have

$$\begin{aligned} \hat{l}_z Y_l^{m_l}(\theta, \varphi) &= \left( -i\hbar \frac{\partial}{\partial\theta} \left[ \frac{1}{\sqrt{2\pi}} e^{im_l\theta} \right] \right) \Phi_l^{m_l}(\varphi) \\ &= \frac{\hbar m_l}{\sqrt{2\pi}} e^{im_l\theta} \Phi_l^{m_l} \\ &= \hbar m_l \Theta_l \Phi_l^{m_l} = \hbar m_l Y_l^{m_l}(\theta, \varphi) \end{aligned} \quad (14.5.5)$$

and therefore  $Y_l^{m_l}(\theta, \varphi)$  are eigenfunctions of the operator  $\hat{l}_z$ .

We've seen that the wave functions  $Y_l^{m_l}(\theta, \varphi)$  are eigenfunctions of all of  $\hat{H}$ ,  $\hat{l}^2$ , and  $\hat{l}_z$ . Therefore, all three of these operators share a common set of eigenfunctions and all three of these quantities commute and their eigenfunctions can be known exactly and simultaneously. In other words, the total energy, magnitude of the angular momentum, and  $z$  component of the angular momentum vector can be known simultaneously. So, we can know the length of the angular momentum vector and one of its components (the  $z$  component), but the other two components (the  $x$  and  $y$  directions) remain a mystery. Stated more concisely, the length and direction of the angular momentum cannot be known simultaneously.

In Equation (14.5.1) we saw that the magnitude of the angular momentum vector is  $|\vec{l}| = \hbar\sqrt{l(l+1)}$ . In

Equation (14.5.5) we found that the magnitude of the angular momentum in the  $z$  direction is  $l_z = m_l \hbar$ . Since  $l_z$  is known exactly, we require that the angular momentum vector  $\vec{l}$  *not lie along the  $z$  axis*. If this were the case, the  $x$  and  $y$  components of the angular momentum would be zero and therefore known which is in direct contradiction to the uncertainty principle.

The uncertainty in the  $x$  and  $y$  components of the angular momentum give rise to what is known as the *vector model of angular momentum*, a model which provides information about all possible values of the quantum number  $m_l$  for a given value of  $l$ . A depiction of this model is shown in Figure 14.4.

Knowing the magnitude of the angular momentum vector allows all of the  $x$ ,  $y$ , and  $z$  components of the vector to vary *in a way that constrains the position of the vector to defining the surface of a sphere*. Knowing the orientation of the vector in the  $z$  direction, however, and remembering that angular momentum is quantized, *limits these surfaces to being conical*.

We can rationalize these three-dimensional results more concretely by doing some math. For instance, suppose that the magnitude of the angular momentum is known for a given value of  $l$  such that  $|\vec{l}|^2 = \hbar^2 l(l+1)$ . With no further knowledge about the components of the vector, we know immediately that

$$|\vec{l}|^2 = \hbar^2 l(l+1) = l_x^2 + l_y^2 + l_z^2 \quad (14.5.6)$$

which is the equation of a sphere of radius  $\hbar^2 l(l+1)$ . Now, further suppose that we measure the  $z$  component of the angular momentum and determine that  $l_z^2 = \hbar^2 m_l^2$  so that we can rewrite Equation (14.5.6) as

$$|\vec{l}|^2 - l_z^2 = l_x^2 + l_y^2 \quad (14.5.7)$$

$$\hbar \sqrt{l(l+1) - m_l^2} = \sqrt{l_x^2 + l_y^2} \quad (14.5.8)$$

where (14.5.7) defines the circle at the apex of the cone and (14.5.8) defines the conical surface seen in Figure 14.4. The surface is defined in the second equation because  $l_x^2$  and  $l_y^2$  are completely unknown and therefore can take on any values which satisfy quantization and Equation (14.5.8). Figure 14.4 also provides some intuition for the correspondence principle; for any given value of the quantum number  $l$ , there are  $2l+1$  values of  $m_l$  and therefore the number of cones increases linearly with  $l$ . For large enough  $l$ , the cones get closer and closer until merging into a sphere, as we would see in the classical case, as mentioned above.

The quantization of the  $z$  component of the angular momentum gives rise to *spatial quantization*, the phenomenon whereby the angular momentum vector can take on only certain orientations in space.

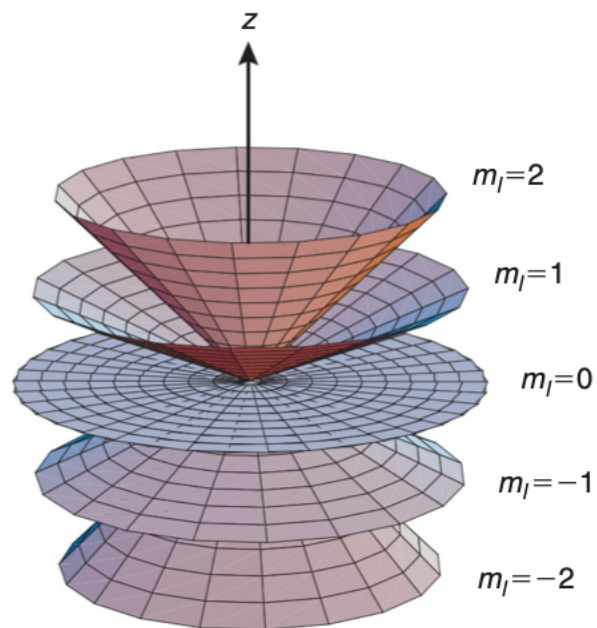


Figure 14.4: The vector model of angular momentum for the quantum number  $l = 2$ . The  $z$  component of the angular momentum is shown in units of  $\hbar$ . The conical shape results from knowing the magnitude of the angular momentum and one of the components of the angular momentum vector while the other two components remain completely unknown.



## CHAPTER

# 15

# VIBRATIONAL AND ROTATIONAL SPECTROSCOPY OF DIATOMICS

### *Rotations*

- *Scientist*

Spectroscopy may be considered the primary application of quantum mechanics. It is the study of interaction between matter and electromagnetic radiation as a function of frequency or wavelength. Nuclear magnetic resonance (NMR), infrared (IR), and Raman spectroscopy are all common tools used by scientists to characterize and visualize the atomic and molecular structure of matter.

Spectroscopic techniques are based upon the transitions between energy states of molecules when they interact with electromagnetic radiation. In particular, because quantum mechanical maintain a discrete energy spectrum, absorption and emission spectra are composed of individual peaks, each of which is associated with a specific transition between two energy levels. As we saw way back in Section 10, energy which is absorbed or emitted by a quantum mechanical system is quantized in units of  $h\nu$  for some frequency  $\nu$ . That is, the energy level spacing between  $E_2$  and  $E_1$  is  $E_2 - E_1 = h\nu$ .

The spacing between energy levels is smallest for NMR spectroscopy, followed by rotational spectroscopy and then vibrational spectroscopy, and lastly electronic spectroscopy which has measures systems with very large spacings between energy levels. These types of spectroscopy use electromagnetic radiation in the form of radio waves, microwaves, infrared, and visible light and beyond, respectively.

As we'll see, not all transition between energy levels may occur, i.e., a transition from  $E_j$  to  $E_i$  may not be allowed. *Selection rules* will tell us which transitions will be experimentally observed.

## 15.1 Absorption, Spontaneous Emission, and Stimulated Emission

*Absorption, spontaneous emission, and stimulated emission* are the basic processes by which transitions between energy levels may occur. Absorption and stimulated emission are initiated by photons from an some external electromagnetic radiation. In contrast, spontaneous emission is a random event related to the lifetime of the excited state (as the name implies). By the uncertainty principle we know that energy and time are conjugate

variables so that  $\Delta E \Delta t \geq \hbar/2$ . So, for spectroscopic techniques which operate at lower frequencies on the electromagnetic spectrum, the change in energy required to initiate the transition is lower and therefore the lifetime in the excited state is higher. That is, when  $\Delta E$  gets smaller  $\Delta t$  must get larger to compensate.

Spontaneous emission and stimulated emission differ in a very important respect. Since spontaneous emission is a completely random process, the emitted photons are *incoherent*, meaning that their phase angles are completely random. In contrast, the photons of stimulated emission are *coherent* and propagate in the same direction as the photons which caused excitation in the first place. For example, a light bulb is an incoherent source of photons and the intensity of the emitted light falls off with the square of the distance from the source. In contrast, a laser is a coherent source of radiation and is the reason that lasers can maintain such high intensity even when reflected from a very far distance, such as the windows of a plane.

Models for the three types of transitions are shown in Figure 15.1.  $B_{12}$ ,  $B_{21}$ , and  $A_{21}$  represent proportional constants for absorption, stimulated emission, and spontaneous emission, respectively. Each of the transitions is directly proportional to the radiation density  $\rho(\nu)$  as a function of the incident frequency  $\nu$  of the electromagnetic radiation, as well as the population of the energy level,  $N_1$  for  $E_1$  and  $N_2$  for  $E_2$ . The proportionality with population of the energy state should make sense: if there are no atoms or molecules in the  $E_1$  state then there is no way for a atom or molecule to be excited to the  $E_2$  state, for example.

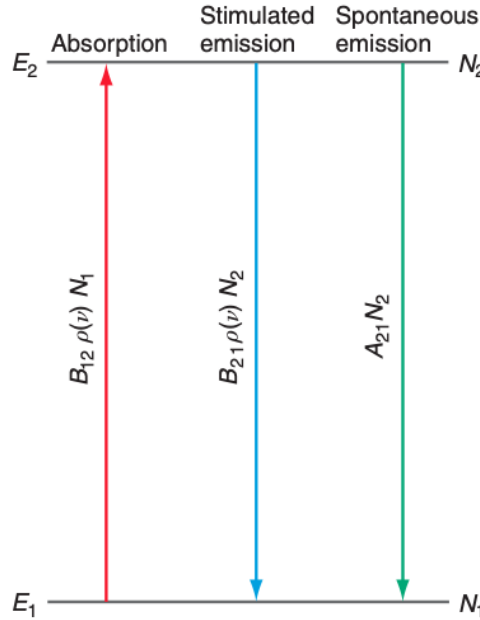


Figure 15.1: Model for absorption, spontaneous emission, and stimulated emission. The rate at which transitions between levels occurs is directly proportional to the population of the energy levels,  $N_1$  and  $N_2$  for absorption and emission, respectively, and the radiation density as a function of frequency,  $\rho(\nu)$ .

At equilibrium, the transition rate between the energy levels must be equal such that

$$B_{12}N_1\rho(\nu) = B_{21}N_2\rho(\nu) + A_{21}N_2 \quad (15.1.1)$$

Moreover, the ratio of the populations in either energy level should follow a Boltzmann distribution, defined in Equation (10.8.3), such that

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-|E_2 - E_1|/k_B T} = e^{-h\nu/k_B T}$$

where  $g_2$  and  $g_1$  are degeneracies of each state and taken to be equal because in our example there is no preference to be in either energy level. Note that under the assumption that neither energy level is preferred

over the other we can deduce that  $B_{12} = B_{21}$ . Then, we can rewrite Equation (15.1.1) as

$$\begin{aligned}\frac{N_1}{N_2} &= \frac{B_{21}\rho(\nu) + A_{21}}{B_{12}\rho(\nu)} \\ \left(e^{-h\nu/k_B T}\right)^{-1} &= \frac{B_{21}}{B_{12}} + \frac{A_{21}}{B_{12}\rho(\nu)} \\ e^{h\nu/k_B T} &= 1 + \frac{A_{21}}{B_{12}\rho(\nu)} \\ A_{21} &= \left(e^{h\nu/k_B T} - 1\right) B_{12}\rho(\nu)\end{aligned}$$

Here, recall the Planck distribution law for blackbody radiation, derived in Equation (10.3.2). We can substitute this result for the radiation density in the expression above:

$$\begin{aligned}\frac{A_{21}}{B_{12}} &= \left(e^{h\nu/k_B T} - 1\right) \left(\frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1}\right) \\ \frac{A_{21}}{B_{12}} &= \frac{8\pi h\nu^3}{c^3} = \frac{16\pi^2 \hbar \nu^3}{c^3}\end{aligned}\tag{15.1.2}$$

Equation (15.1.2) offers a ratio of the rate of spontaneous emission to absorption. This relationship will have implications in the lifetimes of excited states. Note that since  $B_{12}$ ,  $B_{21}$ , and  $A_{21}$  are effectively rate constants, their inverses define a lifetime. So, since  $A_{21} \sim \nu^3$ , the lifetime of the excited state is  $T \sim 1/\nu^3$ .

## 15.2 Selection Rules

All types of spectroscopy have selection rules which govern the allowed transitions that can occur between different energy levels. The *transition dipole moment*, denoted  $\mu_{mn}$ , is used to determine whether transitions are allowed under an electric dipole interaction. Just as we think of a dipole moment as being the permanent separation of charge within a molecule, the transition dipole moment is the separation of charge within a molecule *associated with the transition between two states*. In general,  $\mu_{mn}$  is a complex vector whose direction gives the polarization of the transition and whose magnitude squared gives the strength of interaction with a source of electromagnetic radiation.

The transition dipole moment satisfies the condition

$$\mu_{mn}(x) = \int_{-\infty}^{\infty} \psi_m^*(x) \mu_x(x_e + x) \psi_n(x) dx \neq 0\tag{15.2.1}$$

where  $x$  is the vibrational amplitude and  $\mu_x$  is the dipole moment along the direction of the electric field, in which the  $x$  direction is chosen here. Since the dipole moment of a molecule varies with vibrations, there is both a permanent dipole,  $\mu^0$ , (granted, it might be zero) and dynamic dipole,  $\mu(x)$ , within any molecule of spectroscopic interest. Since the amplitude of vibration is a periodic function of  $x$ , by Taylor's theorem we can expand  $\mu(x)$  into a power series centered at the equilibrium bond length  $x_e$ . Also, because  $x$  is the vibrational amplitude,  $x_e$  corresponds to a displacement of zero:

$$\begin{aligned}\mu_{mn}(x_e + x(t)) &= \mu^0 + [x(t) - x_e] \left(\frac{d\mu_x}{dx}\right)_{x=0} + [x - x_e]^2 \left(\frac{d^2\mu_x}{dx^2}\right)_{x=0} + \dots \\ &= \mu^0 + x(t) \left(\frac{d\mu_x}{dx}\right)_{x=0} + x^2(t) \left(\frac{d^2\mu_x}{dx^2}\right)_{x=0} + \dots\end{aligned}$$

Substituting Equation (15.2.1) into this expression affords

$$\begin{aligned}\mu_{mn}(x_e + x(t)) &= \int_{-\infty}^{\infty} \psi_m^*(x) \mu^0 \psi_n(x) dx \\ &\quad + \int_{-\infty}^{\infty} \psi_m^*(x) \left[ x \left( \frac{d\mu_x}{dx} \right)_{x=0} \right] \psi_n(x) dx \\ &\quad + \int_{-\infty}^{\infty} \psi_m^*(x) \left[ x^2 \left( \frac{d^2\mu_x}{dx^2} \right)_{x=0} \right] \psi_n(x) dx + \dots\end{aligned}$$

In most adsorption experiments, it is reasonable to assume that only the  $n = 0$  energy level is populated. So, we'll now consider the transition dipole moment from the ground state  $n = 0$  to some excited state  $m = m$ . Using Equation (14.2.3), which offers the wave functions for the quantum mechanical harmonic oscillator, we can rewrite this expression for a quantum mechanical harmonic oscillator as

$$\begin{aligned}\mu_{m0}(x_e + x(t)) &= \int_{-\infty}^{\infty} \left( A_m \mathcal{H}_m(\alpha^{1/2}x) e^{-\alpha x^2/2} \right) \mu^0 \left( A_0 \mathcal{H}_0(\alpha^{1/2}x) e^{-\alpha x^2/2} \right) dx \\ &\quad + \left( \frac{d\mu_x}{dx} \right)_{x=0} \int_{-\infty}^{\infty} \left( A_m \mathcal{H}_m(\alpha^{1/2}x) e^{-\alpha x^2/2} \right) x \left( A_0 \mathcal{H}_0(\alpha^{1/2}x) e^{-\alpha x^2/2} \right) dx + \dots \\ &= \mu^0 A_m A_0 \int_{-\infty}^{\infty} \mathcal{H}_m(\alpha^{1/2}x) \mathcal{H}_0(\alpha^{1/2}x) e^{-\alpha x^2} dx \\ &\quad + A_m A_0 \left( \frac{d\mu_x}{dx} \right)_{x=0} \int_{-\infty}^{\infty} \mathcal{H}_m(\alpha^{1/2}x) x \mathcal{H}_0(\alpha^{1/2}x) e^{-\alpha x^2} dx + \dots\end{aligned}\tag{15.2.2}$$

The series above was truncated at the quadratic term because the contributions to the transition dipole moment beyond that are negligible. The first integral in the expression is zero because the Hermite polynomials are orthogonal. Therefore, their product over an integral of all the real numbers is zero. Thus, *the permanent dipole moment of a molecule is not relevant for the absorption of infrared radiation*. Because the dynamic dipole is all that contributes to infrared excitation, homonuclear diatomic molecules do not absorb infrared radiation.

The second integral *will be* zero if the same condition is met. Since we are integrating over a symmetric interval in the second term, the sum will evaluate to zero if and only if the integrand is an odd function in  $x$ , that is, it's asymmetric. As mentioned earlier when the Hermite polynomials were introduced, the  $\mathcal{H}_n(u)$  is an odd function for odd  $n$  and an even function for even  $n$ . Hence, the second integral above contains an odd integrand if and only if  $\mathcal{H}_m$  is an even function which requires that  $m$  be even. The condition introduced in Equation (15.2.1) requires that the transition dipole moment be nonzero in order for a spectroscopic transition to occur and therefore the allowed transitions are those for which  $m$  is odd in Equation (15.2.2).

Thus, only transitions of the kind  $n = 0 \rightarrow m = 2k + 1$  for  $k = 0, 1, 2, \dots$  will afford nonzero transition dipole moments and therefore allow for an energy level transition.

There's a catch, however. If we analyze the integrands of  $\mathcal{H}_m x \mathcal{H}_0$  more closely in Equation (15.2.2), we find that the area under these curves is nonzero *only* for the case of  $m = 1$ . Figure (15.2) illustrates this point. It can be shown most generally that the selection rule is  $\Delta n = \pm 1$  for absorption and emission, respectively.

## 15.3 Vibrational Spectroscopy

In any type of spectroscopy, transitions occur between adjacent energy levels. At room temperature, the number of molecules in the vibrational ground state far exceeds the number molecules in the first vibrational excited state so that the primary transition observed is that from the  $n = 0$  level to the  $n = 1$  level. This corresponds to an  $\Delta n = +1$  transition.

The high sensitivity of modern instrumentation, however, allows us to carry out vibrational spectroscopic experiments for  $\Delta n = +2, +3, \dots$  transitions. These *overtone* transitions are useful because they allow us to determine the extent to which the anharmonic potential of a quantum mechanical oscillator differs the harmonic

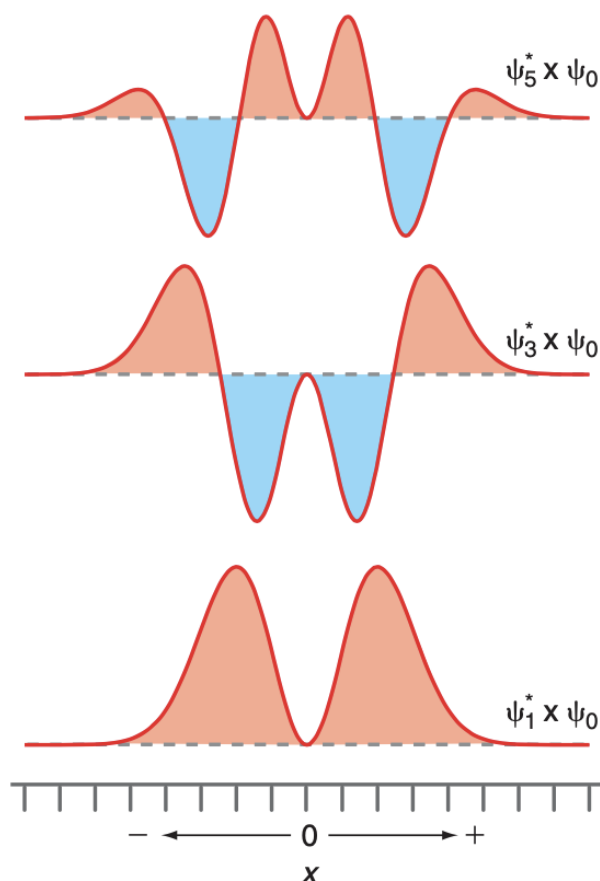


Figure 15.2: The integrand  $\mathcal{H}_m x \mathcal{H}_0$  graphed for  $m = 1, 3$ , and  $5$ . The dashed line indicates zero.

potential of a classical oscillator. A common and fair approximation for the anharmonic potential is describe by the *Morse potential*,

$$V(x) = D_e \left[ 1 - e^{-\alpha(x-x_e)} \right]^2 \quad (15.3.1)$$

where  $x_e$  is the displacement at equilibrium,  $D_e$  is the dissociation energy relative to the bottom of the potential and  $\alpha = \sqrt{k/(2D_e)}$  is a constant dependent on the force constant  $k$ . The Morse potential introduces a new term to the total energy of a quantum mechanical oscillator such that Equation (14.2.6) may be rewritten as

$$E = h\nu \left( n + \frac{1}{2} \right) - \frac{(h\nu)^2}{4D_e} \left( n + \frac{1}{2} \right)^2 \quad (15.3.2)$$

where the second term corrects for the anharmonic potential energy. The selection rule  $\Delta n = +1$  is not rigorously followed for an anharmonic potential so that transitions of  $\Delta n = +2, +3, \dots$  can be observed from the  $n = 0$  ground state. These *overtone* transitions are much weaker than the  $n = 0 \rightarrow n = 1$  transition but can be measured with sensitive enough instrumentation.

## 15.4 Rotational Spectroscopy

As for the quantum harmonic oscillator, the selection rule  $\Delta J = \pm 1$  governs the absorption of electromagnetic radiation for the quantum mechanical rotor. Importantly, note that the quantum number  $l$  is being represented as  $J$  here.  $l$  usually denotes the *orbital angular momentum* in three dimensions whereas  $J$  is used for the angular momentum of rotating molecules, those restricted to two dimensions.

In contrast to vibrational spectroscopy which requires that a molecule have a dynamic dipole, a permanent

dipole is required for a molecule to absorb energy in the microwave portion of the electromagnetic spectrum and therefore be rotationally excited. As we saw in Equation (14.4.18) in the Section regarding the three-dimensional quantum rigid rotor, the dependence on the energy of the quantum rotor on the quantum number  $J$  (formerly known as  $l$ ) may be written

$$E_J = \frac{\hbar^2}{2I} J(J+1) = \frac{\hbar^2}{2\mu\rho_0^2} J(J+1) = \frac{h^2}{8\pi^2\mu\rho_0^2} J(J+1) = hcBJ(J+1) \quad (15.4.1)$$

where  $B = h/(8\pi^2c\mu\rho_0^2)$  is the *rotational constant* and is dependent on the reduced mass  $\mu$  and radial distance between the atoms  $\rho_0$ . The factor of  $c$  (the speed of light) is included in  $B$  to give it units of  $\text{cm}^{-1}$  rather than  $\text{s}^{-1}$ , similar to the wave number  $\tilde{\nu}$  used in infrared spectroscopy.

We can begin a discussion on rotational spectroscopy by first considering the spacings between energy levels. For a transition from energy level  $J$  to  $J+1$ ,

$$\begin{aligned} \Delta E &= E_{J+1} - E_J \\ &= hcB(J+1)(J+2) - hcBJ(J+1) \\ &= hcB(J^2 + 3J + 2 - J^2 - J) \\ &= hcB(2J + 2) \\ &= 2hcB(J + 1) \end{aligned} \quad (15.4.2)$$

Thus, we see that the energy gap between allowed absorptions is  $E \sim (2J+1)B$  with a proportionality constant of  $hc$ . The inclusion of  $B$  in this proportionality is to reinforce the point that  $B$  is *molecule specific since it depends on the reduced mass and bond length of the diatomic*.

Now we consider the change in energy during emission, from energy level  $J$  to  $J-1$ :

$$\begin{aligned} \Delta E &= E_{J-1} - E_J \\ &= hcB(J-1)J - hcBJ(J+1) \\ &= hcB(J^2 - J - J^2 - J) \\ &= -2hcBJ \end{aligned} \quad (15.4.3)$$

Thus, the energy gap between allowed emissions is  $|E| \sim 2BJ$  with the same proportionality constant as above. Note that the difference in energy between absorption and emission are different because energy levels are not equally spaced.

Since the energy required for absorption is greater than that of emission, the naive student may assume that the majority of the molecules in a collection occupy energy levels corresponding to smaller values of  $J$ . So, we can ask ourselves, how many molecules are there in states for a given value of  $J$  relative to the ground state  $J=0$ ? To get an idea of the answer we can use the Boltzmann distribution:

$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-(E_J - E_0)/k_B T} = (2J+1) e^{-\hbar^2 J(J+1)/(2Ik_B T)} \quad (15.4.4)$$

Here,  $n_J$  and  $n_0$  represent the number of particles in the  $J$ th excited state and the ground state, respectively, and  $g_J$  and  $g_0$  are their respective degeneracies. We take  $E_0$  to be the zero point energy and therefore the difference  $E_J - E_0$  becomes the energy of the  $J$ th energy level. Lastly, Equation (14.4.18) was used to substitute an expression for the energy levels within the exponential.

Most importantly, the degeneracy of the rotational ground state energy is 1, whereas the degeneracy of energy level  $J$  is always  $2J+1$ . This degeneracy term generally dominates the ratio  $n_J/n_0$  for small  $J$  and sufficiently large temperatures. As  $J$  increases, however, the exponential term causes  $n_J/n_0$  to rapidly decrease.

Additionally, for molecules with a large enough moment of inertia the exponential term does not heavily influence the ratio until  $J$  is quite large. As a result, many rotational energy levels are occupied. In contrast,

molecules with a small moment of inertia tend to populate far fewer rotational energy levels because the exponential term of Equation (15.4.4) has a greater influence on the ratio  $n_J/n_0$ . A plot of the Boltzmann distribution for different temperatures is shown in Figure 15.3.

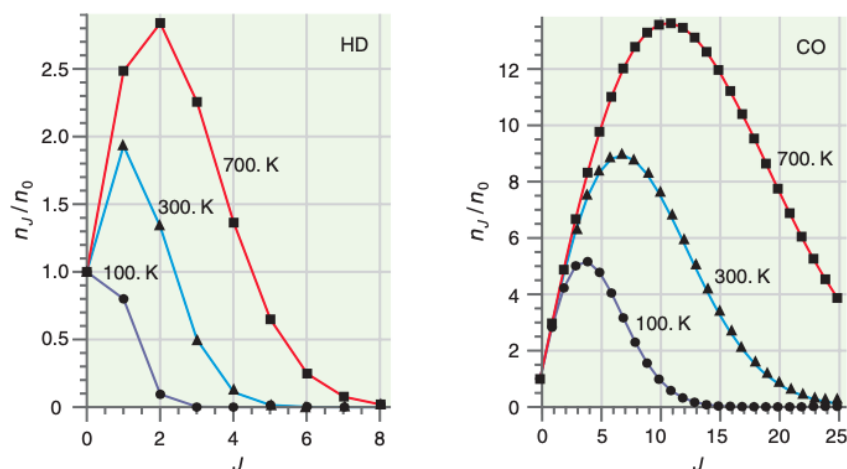


Figure 15.3: A plot of the Boltzmann distribution for  $\text{CO}_2$  for the occupation of rotational energy levels corresponding to the quantum number  $J$  for different temperatures.

For a microwave spectroscopy experiment, we'd expect the relative absorption of each of the energy states to follow a pattern similar to that of Figure 15.3 above. This spectrum is illustrated below, in Figure 15.4.

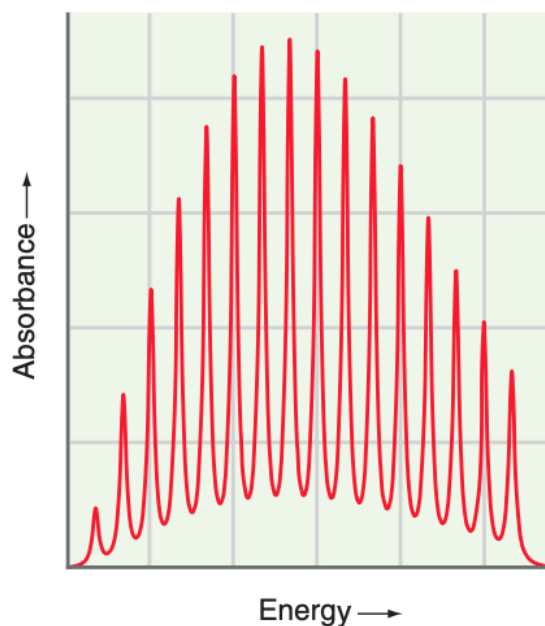


Figure 15.4: The spectrum observed through microwave radiation of  $\text{CO}_2$ . The shape of this spectrum behaves similarly to that of Figure 15.3 which delineates the relative occupation of each energy level.

## 15.5 Rotational Spectroscopy

## CHAPTER

# 16

## HYDROGEN

*Hydrogen*

- *Scientist*

The hydrogen atom serves as a prototype for more complex atoms and, therefore, molecules. Firstly, the wave functions of an electron within a hydrogen atom, also known as a hydrogen atomic orbital, will be studied and we'll see that the familiar set of orbitals studied in general chemistry arise naturally as solutions to the Schrödinger equation.

### 16.1 The Schrödinger Equation for Hydrogen

For atoms with more than a single electron, the Schrödinger equation cannot be solved exactly. In contrast, the wave function which describes the electron of hydrogen can be determined exactly and serves as a starting point to try and find (near) exact solutions for the Schrödinger equation describing many electron atoms.

We can begin by modeling a hydrogen atom as having a nucleus at the center of some coordinate system and an electron moving about space around the nucleus. The two particles are attracted to one another with a potential energy given by the *Coulombic potential*,

$$V(r) = -\frac{q_e^2}{4\pi\epsilon_0 r} = -\frac{kq_e^2}{r}$$

where  $q_e$  is the charge of an electron (and a proton, hence  $q_e^2$  cause the total charge is the product of the charge on the electron and the proton),  $\epsilon_0$  is the permittivity of a vacuum,  $r$  is the radial distance between the two particles, and  $k = 1/4\pi\epsilon_0$  is a constant to make things more neat.<sup>1</sup> Since this potential is spherically symmetric we'll formulate the Schrödinger Equation in spherical coordinates. In doing so, we arrive at the

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<sup>1</sup>The factor of  $4\pi\epsilon_0$  arises in this expression because units of all quantities are chosen to be in SI.



following expression for the Schrödinger equation:

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(\rho, \theta, \varphi) + V(r)\psi(\rho, \theta, \varphi) = E\psi(\rho, \theta, \varphi)$$

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\psi}{\partial\rho}\right) + \frac{1}{\rho^2\sin^2\varphi}\frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{\rho^2\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\psi}{\partial\varphi}\right)\right] + V(r)\psi = E\psi \quad (16.1.1)$$

Note that  $\rho$  is the radial distance between the electron and the nucleus,  $\theta$  is the polar (azimuthal) angle, and  $\varphi$  is the zenith angle. While (16.1.1) appears unwieldy at first glance, we can bring it into a more manageable and even recognizable form with a little bit of ingenuity. Firstly, multiply through by a factor of  $2m_e\rho^2$  to afford

$$-\hbar^2\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\psi}{\partial\rho}\right) - \hbar^2\left[\frac{1}{\sin^2\varphi}\frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\psi}{\partial\varphi}\right)\right] + 2m_e\rho^2[V(r) - E]\psi = 0 \quad (16.1.2)$$

which is more clearly an equation with two principle components, one with a dependence on only  $\rho$  and the other with a dependence on  $\theta$  and  $\varphi$ . Recall that we define the operator  $\hat{L}^2$  as

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin^2\varphi}\frac{\partial^2\psi}{\partial\theta^2} + \frac{1}{\sin\varphi}\frac{\partial}{\partial\varphi}\left(\sin\varphi\frac{\partial\psi}{\partial\varphi}\right)\right]$$

which is exactly what we see in (16.1.2) so that it can be rewritten as

$$-\hbar^2\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial\psi}{\partial\rho}\right) + \hat{L}^2\psi + 2m_e\rho^2[V(r) - E]\psi = 0 \quad (16.1.3)$$

Additionally, we know that solutions to  $\psi$  can be written as a product of functions, namely  $\psi = R(r)\Theta(\theta)\Phi(\varphi)$ , and that the angular portion of  $\psi$  must be a spherical harmonic of the form  $Y_l^{m_l}(\theta, \varphi)$ , defined earlier. Recall that  $Y_l^{m_l}(\theta, \varphi)$  is an eigenfunction of the operator  $\hat{L}^2$  and satisfies

$$\hat{L}^2 Y_l^{m_l}(\theta, \varphi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta, \varphi)$$

Ultimately, then, if we substitute  $\psi = R(r)\Theta(\theta)\Phi(\varphi)$  into (16.1.3), we can rewrite the expression as

$$-\frac{\hbar^2}{2m_e\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R(\rho)}{\partial\rho}\right) + \left[\frac{\hbar^2 l(l+1)}{2m_e\rho^2} + V(r) - E\right]R(\rho) = 0 \quad (16.1.4)$$

which is known as the *radial equation* for the hydrogen atom. Substituting the Coulomb potential for  $V(\rho)$  above, the radial equation becomes

$$-\frac{\hbar^2}{2m_e\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R(\rho)}{\partial\rho}\right) + \left[\frac{\hbar^2 l(l+1)}{2m_e\rho^2} - \frac{kq_e^2}{\rho} - E\right]R(\rho) = 0$$

$$-\frac{\hbar^2}{2m_e\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R(\rho)}{\partial\rho}\right) + [V_{\text{eff}}(\rho) - E]R(\rho) = 0 \quad (16.1.5)$$

where we define the *effective potential* as

$$V_{\text{eff}}(\rho) = \frac{\hbar^2 l(l+1)}{2m_e\rho^2} - \frac{kq_e^2}{\rho} \quad (16.1.6)$$

The effective potential is made up of two components: a *centrifugal potential* which varies as  $+1/r^2$  and a coulombic potential which varies as  $-1/r$ . The centrifugal potential is positive and corresponds to a repulsive interaction between the electron and nucleus within a hydrogen atom; it dominates at small distance if  $l \neq 0$ , that is, for all orbitals aside from the  $s$  orbitals. In contrast, the coulombic potential is negative and is associated with attractive interactions. Although both terms within the effective potential go to zero as the distance between the electron and proton go to infinity, the coulombic potential decreases less quickly so that there is minimum effective potential which corresponds to the most probable distance between the electron and

nucleus within a hydrogen atom. A plot of the effective potential as a function of the distance between the nucleus and electron is illustrated in Figure 16.1.

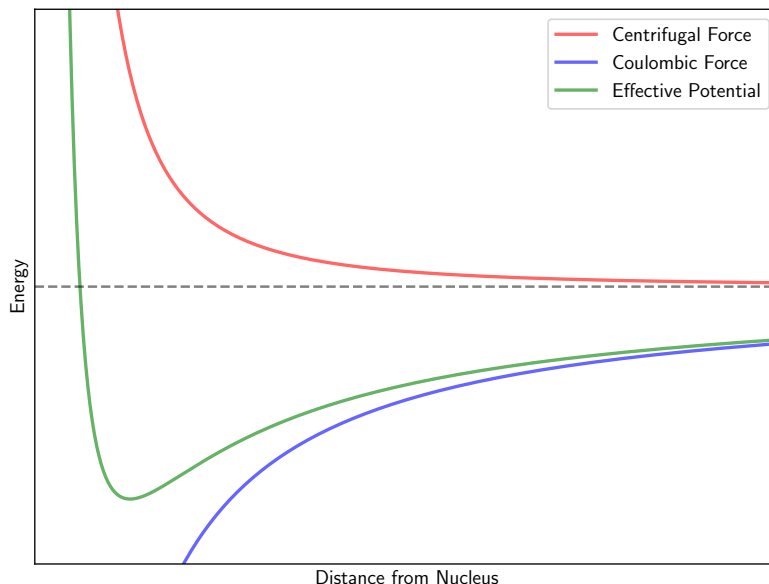


Figure 16.1: Plot of the centrifugal, coulombic, and effective potentials. As is clear, the centrifugal force dominates at smaller interatomic distances while the coulombic potential at larger distances.

### 16.1.1 Eigenvalues and Eigenfunctions of the Hamiltonian

Equation (16.1.4) has the direct physical interpretation that the total energy  $E$  is the sum of the radial kinetic energy, an angular kinetic energy, and a potential energy. This expression is a first order differential equation which affords the following solution for the total energy:

$$E_n = -\frac{m_e q_e^2}{8\epsilon^2 h^2 n^2}, \quad n = 1, 2, 3, 4, \dots \quad (16.1.7)$$

This quantity is typically rewritten using the Bohr radius (Section 10.7, Equation (10.7.6)),  $a_B = \epsilon_0 h^2 / \pi m_e q_e^2$  to yield

$$E_n = -\frac{m_e q_e^2}{8\epsilon^2 h^2 n^2} = -\frac{2.179 \times 10^{-18} \text{ J}}{n^2} = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 1, 2, 3, 4, \dots$$

In any case, the wave function for the hydrogen atom goes to zero as  $n \rightarrow \infty$  as we'd expect. As a reminder, the zero energy is more of a convention than an actual quantity. Note that although the energy depends only on the principle quantum number  $n$ , the eigenfunctions  $\psi_n$  are associated with three quantum numbers,  $n$ ,  $l$ , and  $m_l$ , to accommodate spatial quantization in three dimensions.

Just as we've done previously, the energy eigenvalue and corresponding eigenfunctions of the total energy operator can be superimposed onto a potential energy diagram to see how the wave function changes with increasing quantum number  $n$ . The potential energy forms a region of confinement for the particles (similar to the box for a particle in a box) which is infinitely deep at the center and whose depth falls off inversely with the distance between the proton and electron.

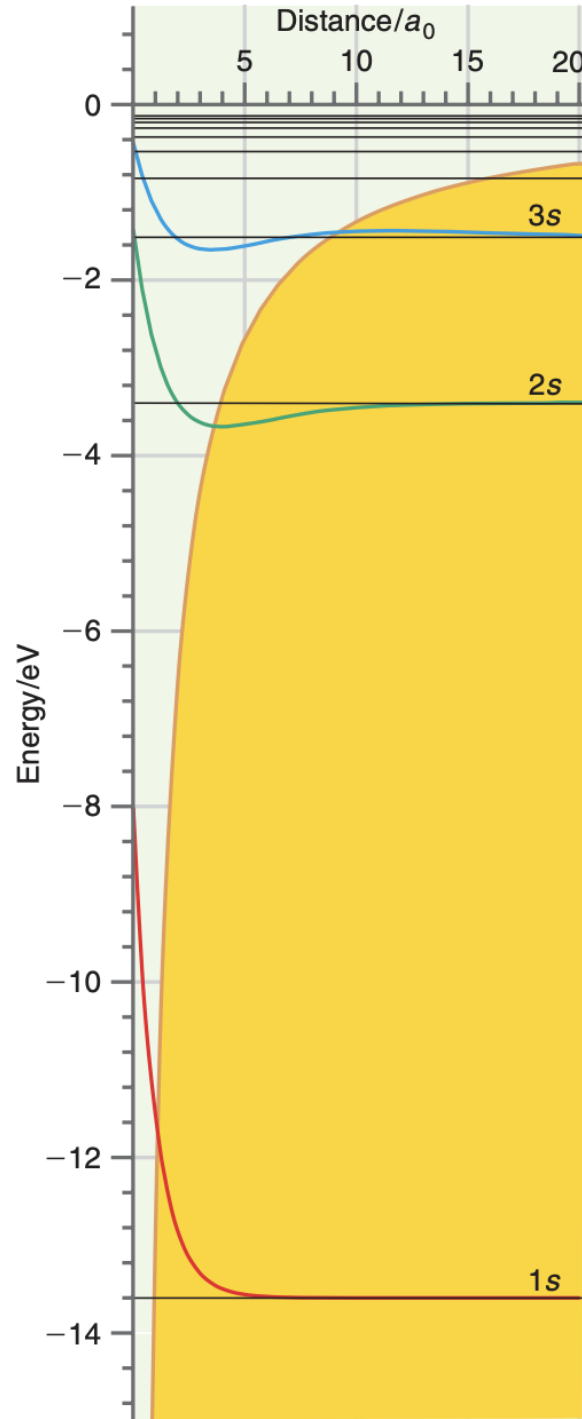


Figure 16.2: Pff

## 16.2 The Hydrogen Atomic Orbitals

The ground state wave function for the hydrogen atom, corresponding to the 1s orbital, may be expressed as

$$\psi_{100}(r) = \left( \frac{1}{\sqrt{\pi}} \right) \left( \frac{Z}{a_B} \right)^{3/2} e^{-Zr/a_B} \quad (16.2.1)$$

where  $Z$  is the effective nuclear charge of that atom and equal to 1 for hydrogen and  $a_B$  is the Bohr radius and is constant, in particular  $a_B = 52.9$  pm. Since  $r = \sqrt{x^2 + y^2 + z^2}$  is a function of three variables, a plot of  $\psi_{100}(r)$  lives in  $\mathbb{R}^4$  and therefore we would need four dimensions to visualize the surface. Instead, we reduce

the dimensionality of the graph by considering a level set of  $\psi_{100}$ . Doing this, we can see clearly that the wave function is maximized at  $r = 0$  (although, note that the distance between the electron and nucleus of hydrogen will never actually reach zero by the uncertainty principle) and falls off exponentially as  $r \rightarrow \infty$ .

Now, suppose we increase the principle quantum number  $n$  and consider the  $2s$  and  $3s$  orbitals of hydrogen. With  $l = 0$  remaining constant, the electron wave function remains a function of only  $r$  and we can ignore  $\theta$  and  $\varphi$ . In contrast to the  $1s$  orbital, however, the  $2s$  and  $3s$  orbitals contain 1 and 2 nodes, respectively. Moreover, since these nodes correspond to particular (constant) values of  $r$ , they represent *spherical nodal surfaces*, rather than nodal points.

Before continuing to the next section, below is the general form of the hydrogen wave function for any combination of quantum numbers  $n$  and  $l$ :

$$\psi_{nl}(r) = R_{nl}(r) = - \left\{ \left( \frac{2Z}{na_B} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} \left( \frac{2Zr}{na_B} \right)^l L_{n+l}^{2l+1}(2Zr/na_B) e^{-Zr/na_B} \quad (16.2.2)$$

Note that  $Z = 1$  for the hydrogen atom and that  $L_q^p(x)$  is the *associated Laguerre polynomial*.

### 16.2.1 The Radial Distribution

Above we began to consider the behavior of wave functions with no angular momentum component, that is, the  $s$  orbitals. If we consider the eigenfunctions of the Hamiltonian for a one electron atom with  $l > 0$ , we can begin to understand the differences between the  $s$  orbitals and the  $p$  and  $d$  orbitals.

Analogous to the  $s$  orbitals, the  $p$  and  $d$  orbitals are best visualized with contour plots, and in particular, contour plots at constant angles for  $\theta$  and  $\varphi$ . It can be shown that the radial component of the energy eigenfunctions for this system have  $n-l-1$  nodes while the angular component has  $l$  nodes, for a total of  $n-1$  nodes, consistent with our models for the particle in a box and the harmonic oscillator.

Continuing with a discussion about orbitals involving nonzero values of the quantum number  $l$ , we consider the probability density  $\psi_{nlm_l}^2(r, \theta, \varphi)$ . As a brief aside, and partial sanity check, for the  $s$  orbital we know already that the probability density will be spherically symmetric and decrease exponentially with the distance from the nucleus. A plot of the eigenfunction in many different ways, each beneficial in their own respect, can be found in Figure 16.3.

It's important to keep in mind that  $\psi^2$ , no matter the quantum numbers, is *normalized*. The normalization integral of  $\psi^2$  must be interpreted as the sum of all electronic charges of all shells of infinitesimal thickness  $dr$  around the nucleus. So, instead of just thinking about  $\psi^2$  as the probability of finding an electron anywhere in space around the nucleus, we should be thinking about  $\psi^2 dv$  as the probability of finding an electron *in a small region of space* around the nucleus. For a spherically symmetric function,  $dv = 4\pi r^2 dr$  so that the radial probability distribution for the ground state electron of a hydrogen atom is

$$P(r)dr = 4\pi r^2 \psi_{100}^2(r)dr \quad (16.2.3)$$

The advantage of this distribution is that it accounts explicitly for both the *charge density* and the *volume* of the electron cloud. Consider, for example, the juxtaposition of the plots in Figure 16.4. Both plots in 16.4a and 16.4b contain two normalized wave functions, though, the latter more clearly illustrates how no matter the atom, the area under the curve is equal to one. Also, with the radial distribution we can more easily pick out the most probable distance away from the nucleus for an electron to be (it's where the distribution peaks).

Figure 16.4 displays only the  $n = 1$   $s$  orbitals for H and  $\text{He}^+$ . To get a vague idea of the radial distribution function for principle quantum numbers greater than 1, consider the radial distribution for the  $2s$  orbital of a

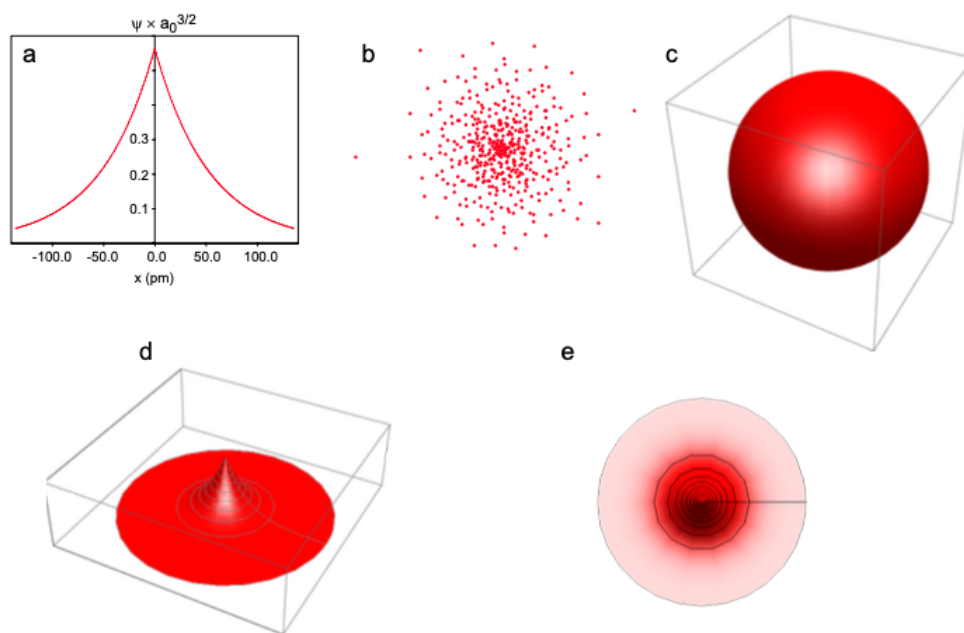
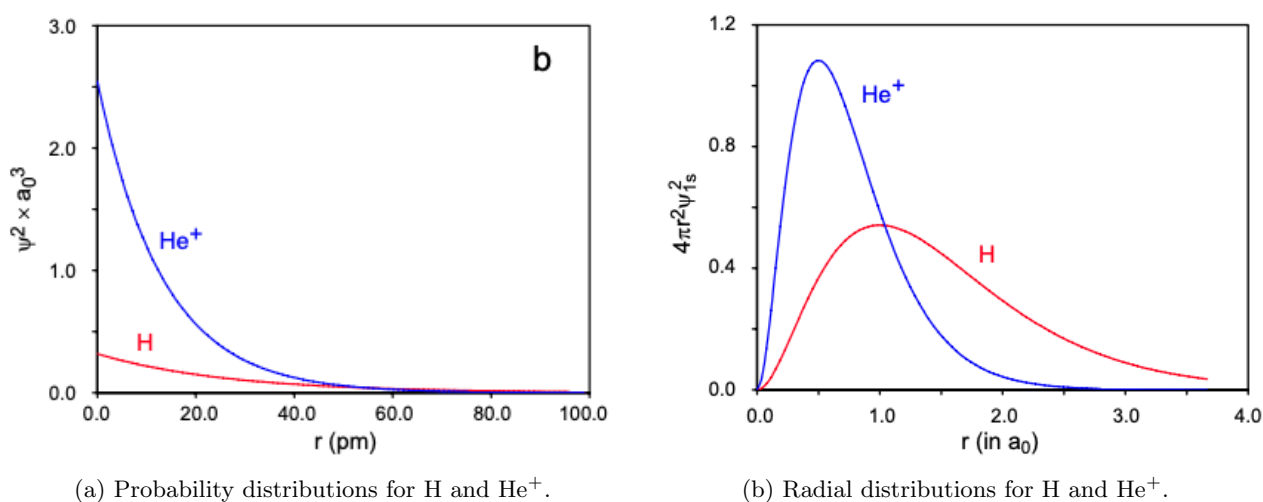


Figure 16.3: (a)  $\psi_{100}(r)$  plotted against  $x$  for a constant  $y$  and  $z$ . (b) A scatter plot of the electron cloud corresponding to the same plot as in (a). (c) The spherical level set of  $\psi_{100}$  for a constant  $r$  such that 95% of the probability is enclosed within the shell. (d) The magnitude of  $\psi_{100}$  plotted as the height above a plane through the nucleus. (e) A contour plot showing the projections of lines obtained from a plot like that of (d) when it is cut by a series of equally spaced planes parallel to the projection plans.



(a) Probability distributions for H and  $\text{He}^+$ .

(b) Radial distributions for H and  $\text{He}^+$ .

Figure 16.4: Difference between the probability distribution and radial distribution for two different one electron systems.

single-electron system:

$$\begin{aligned}
 P_{200}(r) &= 4\pi r^2 \psi_{200}^2(r) dr = 4\pi r^2 \left[ \left( \frac{1}{4\sqrt{2}\pi} \right) \left( \frac{1}{a_B} \right)^{3/2} \left( 2 - \frac{r}{a_B} \right) e^{-r/2a_B} \right]^2 \\
 &= \frac{1}{8a_B^3} \left( 2 - \frac{r}{a_B} \right)^2 r^2 e^{-r/a_B}
 \end{aligned}$$

Clearly, a node appears in the distribution at  $r = 2a_B$ . So, the  $2s$  orbital has one node, in contrast to the  $1s$  orbital which contained none.<sup>2</sup>

<sup>2</sup>We're clearly ignoring the case of the electron occurring at  $r = 0$ , as this corresponds to the situation where the electron is bound directly to the nucleus and therefore has a position and momentum which are exactly known (those being at  $r = 0$  and

Importantly, the unchanged probability distribution and the radial distribution will take a different form when we remove spherical symmetry from the equation, i.e.,  $\ell > 0$ .

### 16.3 Orbital Angular Momentum and Magnetic Moment

Bohr's planetary model of the atom assumed that angular momentum is quantized such that  $L = n\hbar$  for a magnitude of the angular momentum  $L$ . The wave-mechanical solutions described so far have been achieved *without* considering angular momentum. As we'll see, the wave-mechanical solutions to electron orbitals which possess angular momentum do in fact differ from Bohr's predictions.

Recall that Bohr's model of the atom afforded a single quantum number to describe the energy of a quantum mechanical particle. In contrast, wave mechanics yields three quantum numbers to describe the energy of a quantum mechanical particle: the *principle quantum number*  $n$ , the *azimuthal quantum number*  $\ell$  (from which we can determine the magnitude of the orbital angular momentum), and the *magnetic quantum number*  $m_\ell$  (which tells us the  $z$  component of the angular momentum), whose values are limited by  $\ell$ . Notice that the wave-mechanical description of a quantum mechanical particle permits  $\ell = 0$ , i.e., a particle having no angular momentum, something that the Bohr model forbids. As we've seen, the operators for the orbital angular momentum are  $\hat{L}^2$ ,  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$ . The first gives the square of the magnitude, and the next three provide the components along the  $x$ ,  $y$ , and  $z$  axes.

We care about angular momentum because an electron traveling with an angular momentum around a nucleus is a microscopic version of an electric current within a loop, thereby producing a magnetic field perpendicular to the plane of the loop and giving the electron a magnetic moment. The current in the "loop" is given by classical physics,

$$I = -\frac{q_e v}{2\pi r} \quad (16.3.1)$$

where  $2\pi r$  is the circumference of the loop,  $q_e$  is the charge of an electron, and  $v$  is the velocity of the electron. The corresponding magnetic moment vector is  $\mu = IA$  for  $A$  which is the area of the loop enclosed by the electron. Since we already know that the loop is a circle of radius  $r$ ,

$$\mu = IA = -\frac{q_e v r}{2} \quad (16.3.2)$$

If we multiply the top and bottom by the mass of an electron and recognize that  $m_e v r = p_\theta$  for a momentum as a function of the polar angle  $\theta$ , we have

$$\vec{\mu} = -\frac{q_e}{2m_e} \vec{p}_\theta \quad (16.3.3)$$

as the *magnetic moment vector*  $\vec{\mu}$  as a function of the angular momentum vector  $\vec{p}_\theta$ . The strength of a dipole is proportional to the magnitude of the vector  $\vec{\mu}$ :

$$|\vec{\mu}| = \left| -\frac{q_e}{2m_e} \vec{p}_\theta \right| = \frac{q_e \hbar}{2m_e} \sqrt{\ell(\ell+1)} = \mu_B \sqrt{\ell(\ell+1)} \quad (16.3.4)$$

The negative sign of Equation (16.3.3) causes the magnetic moment vector to point in the opposite direction as the angular momentum vector, as a result of the charge of an electron. The quantity  $\mu_B$  is the *Bohr magneton*, and equals  $\mu_B = 9.274 \times 10^{-24} \text{ J/T}$ .

Since it is the orbital angular momentum  $\ell$  which gives rise to a magnetic moment vector (all that stuff we talked about above) we would expect that an electron in the  $1s$ ,  $2s$ ,  $3s$ , etc. orbitals to be unaffected by the presence of a magnetic field. However, experiment has shown the opposite to be true (recall the Stern Gerlach experiment). These results illustrate that another source of a magnetic moment is present within an atom and

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$p = 0$ , respectively), going against the uncertainty principle.

led to the postulate that electrons must spin about an axis in addition to orbiting a nucleus. Hence, we speak of the *electron spin magnetic moment*, in contrast to the orbital angular momentum.

Similar to the orbital angular momentum, the spin angular momentum of an electron can have certain quantized values, separated by a factor of  $\hbar$ . Hence, we use a spin quantum number,  $s$ , analogous to the azimuthal number  $\ell$ , to describe the spin angular momentum. The magnitude of the vector defined by  $s$  is given by  $\sqrt{s(s+1)}\hbar$ . Again, similar to  $\ell$ , we define a quantum number to describe the  $z$  component of the spin angular momentum, denoted  $m_s$ , in analogy to  $m_\ell$ . The allowed values for  $m_s$  range between  $\pm s$ . To round out the picture as a whole, we assume that there exist operators  $\hat{S}^2$ ,  $\hat{S}_x$ ,  $\hat{S}_y$ , and  $\hat{S}_z$  for the spin angular momentum that are analogous to  $\hat{L}^2$ ,  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  for the orbital angular momentum.

For the case of a single-electron system, the situation is simple. Only two spin orientations are possible: the electron can have a spin angular momentum pointing up the  $z$  axis or pointing down the  $z$  axis. The values corresponding to these two situations are respectively  $\pm 1/2$ . This implies that there should be two state functions corresponding to the two spin states of an electrons. Moreover, these should be eigenfunctions of  $\hat{S}_z$  and should have eigenvalues of  $\pm \hbar/2$ .

There are no analytical formulas for the eigenfunctions of  $\hat{S}_z$ , so they are handled symbolically. The spin functions corresponding to  $m_s = 1/2$  and  $m_s = -1/2$  are labelled by  $\alpha$  and  $\beta$  respectively. We assume further that these spins functions form an orthonormal bases such that

$$\int \alpha^* \alpha d\sigma = \int \beta^* \beta d\sigma = 1 \quad \& \quad \int \alpha^* \beta d\sigma = \int \beta^* \alpha d\sigma = 0$$

where  $\sigma$  is some arbitrary spin coordinate to ease integration.

## 16.4 Indistinguishability of Electrons

Unlike macroscopic objects which can be distinguished from one another, any two electrons within an atom cannot necessarily be distinguished from one another. This fact must be taken into account with our formulation of the wave function for an electron.

Suppose we have an  $n$ -electron system which we describe with the wave function  $\psi$  which is a function of the spatial, angular, and spin variables of each of the  $n$  electrons. We know that that wave function itself is not an observable, however, the square of the wave function  $\psi^2$  is proportional to the electron density about the nucleus and therefore may be measured.

Now, consider the helium atom. The two electrons of He are indistinguishable and therefore no observable property of the atom must change upon an exchange of the electrons. Therefore, if we label the electrons as 1 and 2,  $\psi^2(1, 2) = \psi^2(2, 1)$  which is satisfied by either of  $\psi(1, 2) = \psi(2, 1)$  or  $\psi(1, 2) = -\psi(2, 1)$ . If the former is true, the wave function is said to be *symmetric*, whereas if the latter is true the wave function is *antisymmetric*. Functions which do not satisfy either of these properties are *asymmetric* and are not allowable wave functions for a system.

Although both the symmetric and antisymmetric wave functions satisfy the indistinguishability requirement, Wolfgang Pauli showed that only an antisymmetric wave function is allowed for electrons,<sup>3</sup> a result that can be formulated as one of the postulates of quantum mechanics:

*Wave functions describing a many-electron system must change sign (be antisymmetric) under the exchange of any two electrons.*

This postulate is also known as the *Pauli exclusion principle*, or just the *Pauli principle*. This postulate was later extended by Pauli to all fermions (electrons are a type of fermion) in the *spin-statistics theorem*.

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<sup>3</sup>More generally, fermions are classified as particles whose wave functions are antisymmetric under an exchange whereas bosons are classified as particles whose wave functions are symmetric under exchange.

Antisymmetric wave functions can be constructed with ease using a *Slater determinant*:

$$\psi(1, 2, 3, \dots, n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \dots & \phi_m(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \dots & \phi_m(2)\beta(2) \\ \vdots & \vdots & & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \dots & \phi_m(n)\beta(n) \end{vmatrix} \quad (16.4.1)$$

Note that individual electrons are represented by rows in the Slater determinant. Above, the spin functions  $\alpha$  and  $\beta$  alternate going across columns, and  $m = n/2$  if  $n$  is even and  $m = (n + 1)/2$  otherwise. The factor in front of the determinant takes care of normalization. In the preceding formula, the shorthand notation  $\phi_{1s}(1)\alpha(1) = \psi_{nlm_l+1/2}(r_1, \theta_1, \varphi_1, \sigma_1)$  is used to save space.

The beauty of using determinants to formulate wave functions is the relationship between a singular matrix and the physicality of the wave function. If a matrix is singular, its determinant is zero and the inverse matrix cannot be calculated. An interesting fact about matrices is that they are singular whenever two rows or columns of the matrix are linearly dependent, i.e., are the same up to a constant. So, in the case of a Slater determinant, the expression will be zero if any two rows are linearly dependent, i.e., any two electrons can be described by the same set of quantum numbers. By the Pauli principle, no two electrons are allowed to occupy the same set of quantum numbers and therefore the wave function is disallowed. It all makes sense!

A corollary to this result, if not already obvious, is that any given electron orbital, whether it be  $s$ ,  $p$ ,  $d$ , etc., can have *at most* 2 electrons. These electrons are distinguished by their spins.

Note that that set of orbitals with the same values of  $n$  and  $l$  comprise a subshell, and the set of orbitals with the same value of  $n$  comprise a shell.

## 16.5 The Variational Method

A *variational principle* asserts that a problem can be solved using the calculus of variations. The *variational method* is a way of approximating the lowest energy eigenstate, i.e., ground state, and some excited states of a quantum mechanical system by minimizing the expectation of the total energy of the system. Earlier, we saw that electron-electron correlation prohibited us from determining an analytical solution to the Schrödinger equation for systems of more than one electron. So, the variational method allows us to find approximate solutions to the wave functions for such systems and estimate the energies of certain atomic and molecular orbitals.

Consider a system of ground state energy  $E_0$  with a wave function  $\psi_0$  which is known exactly. By the postulates of quantum mechanics, the expectation of the ground state energy can be computed as

$$\langle E_0 \rangle = \frac{\int \psi_0^* \hat{H} \psi_0 d\tau}{\int \psi_0^* \hat{H} \psi_0 d\tau} \quad (16.5.1)$$

where the integration is over all real numbers. Although the total energy operator  $\hat{H}$  can be formulated exactly, the exact total energy  $E_0$  cannot be determined exactly. By the variational principle, no matter which wave function  $\Psi$  we choose to approximate  $\psi_0$ , the ground state energy will always be greater than that of reality. Analytically, this implies that

$$\langle E \rangle = \frac{\int \Psi_0^* \hat{H} \Psi_0 d\tau}{\int \Psi_0^* \hat{H} \Psi_0 d\tau} \geq \langle E_0 \rangle \quad (16.5.2)$$

### 16.5.1 The Hartree-Fock Self-Consistent Field Method

The variational method is frequently used in computational and quantum chemistry calculations. The simplest of these computational methods is the *Hartree-Fock self-consistent field method* (HFSCF).



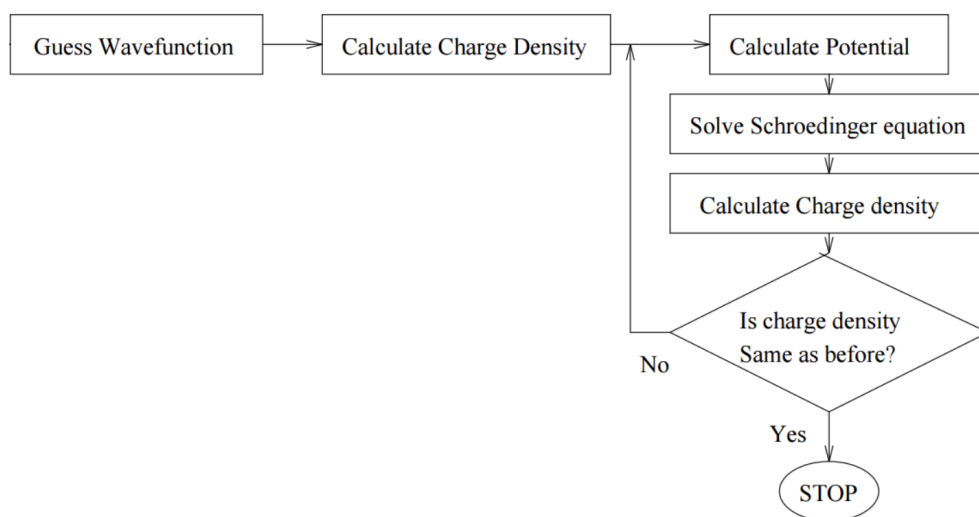


Figure 16.5: An algorithm for computing the wave function of a system using HFSCF.

## CHAPTER

# 17

# QUANTUM STATES FOR MANY-ELECTRON ATOMS

*States for Many electron atoms*

- *Scientist*

Having more than one electron in an atom raises the issue of indistinguishability of electrons, electron spin, and the interaction between orbital and spin magnetic moments. Taking these issues into account leads to a new set of quantum numbers for the states of many-electron atoms and the grouping of these states into levels and terms.

It can be shown that the eigenvalues of a given operator are independent of time only if the operator commutes with the hamiltonian operator. The quantum numbers for hydrogen are *good quantum numbers* because the set of operators  $\hat{l}^2$ ,  $\hat{l}_z$ ,  $\hat{l}_z$ ,  $\hat{s}^2$  and  $\hat{s}_z$  commute with  $\hat{H}$ . In contrast, the good quantum numbers for hydrogen, namely,  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ , do not adequately describe many-electron systems.

Good quantum numbers for many-electron systems are generated by forming vector sums of the orbital and spin angular momenta, where the summation is over the electrons in *unfilled subshells*.

## 17.1 The Helium Atom

## 17.2 Electron Spin

CHAPTER

18

# ATOMIC SPECTROSCOPY

*Atomic*

*- Scientist*

## CHAPTER

# 19

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