 Lectures 5-6

Quantum Mechanics is constructed from a set of postulates about the way microscopic systems behave. These postulates have the same logical role in Quantum Mechanics that axioms do in Mathematics, or laws do in Thermodynamics. Each of these – postulates, axioms, and laws – act as the logical foundation on which the theory is built.

They have different origins, and lead to systems with different bases for truth. In mathematics, axioms are invented, and then the mathematical system is inferred from them. The only basis for truth in mathematics is internal consistency based on logical inferences – i.e. whether a theorem based on the axioms is proven to be a direct consequence of the axioms. There is no basis for deciding on the truth or falsehood of an axiom or of the mathematical system derived from it, as long as that internal consistency exists. As an example, from a mathematical point of view, both Euclidian Geometry, based in part on the idea that parallel lines never meet, is just as true as Riemann Geometry which is based in part on the idea that parallel lines DO meet.

Laws are summaries of experiments, and some of them are used to develop complex theoretical systems, as in the case of Thermodynamics. Unlike axioms, the laws themselves can be proven true or false. There are two bases for this – first, refined experiments may directly demonstrate that the laws are untrue. Second, experiments can demonstrate that logically correct predictions based on the laws are untrue, which logically shows that the laws themselves are untrue. Thus scientific systems based on laws differ from mathematical systems in that internal consistency is no longer sufficient to determine truth or falsehood – successful comparison to an external reality – experimentation – is also necessary.

Postulates are similar to axioms in that they are invented by the theorist. They are different from axioms in that they are invented for the purpose of explaining experimental observations. The postulates themselves are often not directly testable, however. In those cases, they are used to develop a theoretical framework – i.e. to make predictions. These predictions are then compared to experiment. The truth or falsehood of the postulates is then based on the success or failure of the predictions.

It is important to understand this, because a common trap for students first encountering Quantum Mechanics is to try to understand the direct justification for the postulates. This is not possible, since they are not based on direct experience (are not laws), and most certainly are not based on common sense. Remember that common sense is based on the internalization of the direct experience of our senses (hence the name), and the realm of quantum mechanics is in dimensions of size, energy and mass that are too small to be detected by our senses. Thus it is pointless to try to understand where the postulates come from. It is only useful to understand their implications, the way that predictions are based on them, and the truth or falsehood of these predictions.

The first of the **postulates** of quantum mechanics is an expansion of Max Born's explanation of the meaning of $\psi(x)$, and states that the wavefunction $\psi(\mathbf{x})$ **contains all available information about the system**. If the information is not contained in $\psi(x)$, then it is information that quantum mechanics says we cannot obtain.

There are two types of wavefunctions. One type of wavefunction is a wavefunction that is a solution to the Schrödinger equation. These wavefunctions are called eigenfunctions, and have special properties that we will discuss later. The other type of wavefunction is a wavefunction that is not a solution to the Schrödinger equation. In either

case, the wavefunction provides a complete description of the measurable properties of a system. However, in each case, once we've determined the wavefunction that describes a system, we need to learn how to extract the information it contains.

As we have seen, one of the bits of information we can obtain is the energy of our system. We will find that in many cases the solution of the Schrödinger equation yields a set of discontinuous values of the total energy E. In the cases where E is restricted to discontinuous values we say that it is **quantized**. Our first two examples of solving the Schrödinger equation will include one case where the energies are quantized and one where they are not.

Let's return to the Schrödinger equation. If we factor out the $\psi(x)$'s in our Schrödinger equation, we can rewrite it as

$$[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)]\psi(x) = E\psi(x)$$

When the equation is written this way, we can classify it as one of a widely studied class of equations called **eigenvalue equations**. We call the quantity in brackets an **operator**.

An **operator** is a symbol that tells you to perform some action on the variable or function that follows. For example, we can consider the derivative, $\frac{dy}{dx}$, to be the operator, $\frac{d}{dx}$, acting on the variable y. Other examples of operators would be x, for the operation multiply by x, or $\sqrt{}$, for the operation take the square root of. We will denote an operator by a capital letter topped by a carat, like $\hat{A}$. The function, variable or number on which the operator acts is called the **operand**. When we write

$$g(x) = \hat{A}f(x)$$

we mean that g(x) is the function produced when the operator $\hat{A}$ operates on the operand

f(x).

Let's look at a couple of examples of using operators.

Example 1) $\hat{A} = \dfrac{\partial^2}{\partial x^2}$, $f(x) = 2x$. $g(x) = \hat{A}f(x)$. What is g(x)?

$$g(x) = \hat{A}f(x) = \frac{\partial^2}{\partial x^2}(2x) = \frac{\partial}{\partial x}(2) = 0$$

Example 2) $\hat{A} = \dfrac{\partial}{\partial x}$, $f(x,y) = \sin(xy^2)$. $g(x) = \hat{A}f(x)$. What is g(x)?

$$g(x) = \hat{A}f(x) = \frac{\partial}{\partial x}(\sin(xy^2)) = y^2 \cos(x\,y^2).$$

Quantum mechanics uses only a class of operators called **linear, Hermitian operators**. **An operator** $\hat{A}$ **is linear if**

$$\hat{A}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \hat{A}f_1(x) + c_2 \hat{A}f_2(x)$$

In words, this means that an operator is linear if the operator operating on a linear

combination of operands results in the same linear combination of the operator operating

on each individual operand. For example, the operator $\dfrac{d}{dx}$ is linear. To see this, we plug

our operator into the definition and get

$$\frac{d}{dx}[c_1 f_1(x) + c_2 f_2(x)] = c_1 \frac{df_1}{dx} + c_2 \frac{df_2}{dx},$$

which satisfies the condition for a linear operator. It is also useful to note that **a linear**

combination of linear operators is also a linear operator. For example, since $\dfrac{d^2}{dx^2}$

and x are both linear operators, $5\dfrac{d^2}{dx^2}+ix$, a linear combination of the operators, is also a linear operator. Prove this as an exercise.

An example of an operator that is not linear is the operator $\hat{A}$ = square, i.e. the operator that squares a variable. To see this, we plug our operator into our definition of a linear equation and get

$$(c_1f_1+c_2f_2)^2 = c_1^2f_1^2 + 2c_1c_2f_1f_2 + c_2^2f_2^2 \neq c_1f_1^2 + c_2f_2^2.$$

This fails the test for linearity for two reasons – the extra term $2c_1c_2f_1f_2$ and the fact that the operator affected the coefficients c_1 and c_2. The significance of a linear operator is that if an operator is linear, the eigenvalues will be additive, i.e., the eigenvalue of the linear combination of operators making up the linear operator, will be the same linear combination of the eigenvalues of the component operators. As an example, the operator for total energy is called the Hamiltonian operator and is symbolized by $\hat{H}$. $\hat{H}$ is a linear operator. It is the sum of the linear operators for potential and kinetic energy, $\hat{H}=\hat{T}+\hat{V}$. Since it is linear, the eigenvalue for the total energy, E, will be the sum of the eigenvalues of the kinetic energy and potential energy operators, $E=T+V$, where T is the eigenvalue of the kinetic energy operator and V is the eigenvalue of the potential energy operator.

An operator is Hermitian if for two functions ψ_1 and ψ_2

$$\int \psi_1^*(\hat{A}\psi_2)d\tau = \int \psi_2(\hat{A}\psi_1)^* d\tau$$

The reason that quantum mechanical operators must be Hermitian is that **the eigenvalues (solutions) obtained by solving quantum mechanical equations are always real when the operators are Hermitian**. Since we will be using the solutions of our equations to

describe physical observables the requirement that the operators are Hermitian ensures that the results of the equations will be physically meaningful.

As an example of how this equation works, let $\hat{A}$ be the operator $\hat{P}_x = -i\hbar \dfrac{d}{dx}$, the operator for the linear momentum in the x-direction, and let

$$\psi_1(x) = \frac{1}{\pi^{1/4}} e^{-x^2/2} \qquad -\infty < x < \infty$$

and

$$\psi_2(x) = \frac{2^{1/2}}{\pi^{1/4}} xe^{-x^2/2} \qquad -\infty < x < \infty$$

Therefore,

$$\hat{A}\psi_2(x) = -i\hbar \frac{d}{dx} \frac{2^{1/2}}{\pi^{1/4}} xe^{-x^2/2}$$

$$= -i\hbar \frac{2^{1/2}}{\pi^{1/4}} [e^{-x^2/2} - x^2 e^{-x^2/2}]$$

and

$$\int \psi_1^*(x)\hat{A}\psi_2(x)dx = -i\hbar \left(\frac{2}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} (e^{-x^2} - x^2 e^{-x^2})dx$$

$$= -i\hbar \left(\frac{2}{\pi}\right)^{1/2} \left(\pi^{1/2} - \frac{\pi^{1/2}}{2}\right) = \frac{-i\hbar}{2^{1/2}}.$$

Similarly,

$$\hat{A}^*\psi_1(x) = +i\hbar \frac{d}{dx} \frac{1}{\pi^{1/4}} e^{-x^2/2} = -\frac{i\hbar}{\pi^{1/4}} xe^{-x^2/2}$$

and

$$\int \psi_2(x)\hat{A}^*\psi_1^*(x)dx = -i\hbar \left(\frac{2}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-x^2/2}dx$$

$$= -i\hbar \left(\frac{2}{\pi}\right)^{1/2} \frac{\pi^{1/2}}{2} = -\frac{i\hbar}{2^{1/2}}.$$

Thus, we see that $\hat{P}_x$ is Hermitian.

The reason that operators are important in quantum mechanics is that they **allow us to calculate the theoretical values of measurable quantities**. The ability to calculate the values of these measurables depends on **two new postulates** of quantum mechanics. The first, our second postulate, is that **for every observable in quantum mechanics there corresponds a quantum mechanical operator $\hat{A}$**. In a short while we'll show how to construct the operator that corresponds to a given observable.

The immediate question we need to answer now is HOW we use operators to determine the values of the observables. We can use operators to calculate the values of measurable properties because it is possible to write a type of equation, using operators, called an **eigenvalue equation**. For an arbitrary operator, $\hat{A}$, the eigenvalue equation is

$$\hat{A}f(x) = af(x)$$

When we try to solve an eigenvalue equation, we are searching for the function, or set of functions, f(x) which when operated on by $\hat{A}$ yields the original function f(x) multiplied by a constant. We call a function which satisfies an eigenvalue equation an **eigenfunction of the operator $\hat{A}$**, and we call the constant a an **eigenvalue of $\hat{A}$**. In other words, if I have some function f(x) and an operator $\hat{A}$, and I operate on my function with $\hat{A}$, and get back my function times a constant, then my function is an eigenfunction and my constant is an eigenvalue.

Why do we care about eigenfunctions and eigenvalues? This is where our third postulate comes in. It says that **once we know the identity of an operator that**

corresponds to an observable, the only values of that observable which can be measured are the eigenvalues a_i of that operator.

As a first example, the **one dimensional Hamiltonian operator**,

$\hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + V(x)$, is the operator which corresponds to the **total energy** of a particle

moving along the x-axis. Its eigenvalues are the only values of the energy that can be measured. This is exactly the same as saying that these are the only values of the energy that the particle can have.

Our procedure for generating operators will be to first find the expression for the observable we're interested in in classical physics, and then construct its quantum equivalent. To do this we need to generate rules for writing quantum mechanical operators. Let's look at the Hamiltonian as a start. The Hamiltonian operator in quantum mechanics corresponds to a function of classical mechanics also called the Hamiltonian that represents the total energy of a conservative system. The **classical Hamiltonian** is the sum of the kinetic energy T, and the potential energy, V(x), i.e.,

$$H = T + V(x) = \dfrac{p_x^{\,2}}{2m} + V(x)$$

Note that one of the features of the classical Hamiltonian is that the kinetic energy is expressed in terms of the momentum, rather than the velocity. This will also be a feature of the quantum Hamiltonian. By comparing the classical Hamiltonian and the quantum Hamiltonian, we can figure out the quantum operators that correspond to several classical observables. First note that the **potential energy**, V(x) appears in both the classical and quantum Hamiltonians. This must mean that the operator which corresponds to the potential energy is simply the potential energy itself, i.e., $\hat{V} = V(x)$. Since the only other

component of the Hamiltonian is the kinetic energy in the x direction, T_x, the operator for

the **kinetic energy**, $\hat{T}_x = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$. As a final example, if we want to figure out the

operator for the **linear momentum** in the x direction, we note that the classical kinetic

energy is given by $T_x = \dfrac{p_x^{\,2}}{2m}$ and the quantum mechanical kinetic energy is given by

$\hat{T}_x = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$. This suggests that $\hat{p}_x^{\,2} = -\hbar^2\dfrac{\partial^2}{\partial x^2}$ and that therefore $\hat{p}_x = -i\hbar\dfrac{\partial}{\partial x}$.

Comparisons like these lead to the following **rules for generating the operators**

that correspond to various classical observables.

1) **The operator for a position variable, $\hat{q}$, is the position variable itself**. This

is also true for observables that are functions of position only. Thus the operator for

position in the y direction, is $\hat{y} = y$, and the operator for the potential energy in a

conservative system, which is a function of position only, is $\hat{V} = V(x)$.

2) **The operator for momentum, $\hat{p}$, is** $-i\hbar\dfrac{\partial}{\partial q}$, where q indicates a position

variable. For example, the operator for the momentum in the z direction is $\hat{p}_z = -i\hbar\dfrac{\partial}{\partial z}$.

All other operators can be generated as a function of position and momentum

operators. Therefore, we need to learn some **rules for creating functions of operators**.

For the **sum of two operators** we simply have

$$(\hat{A} + \hat{B})f(x) = \hat{A}f(x) + \hat{B}f(x)$$

In other words, added operators function distributively.

Multiplication of operators is accomplished by applying the operators in sequence. In other words

$$(\hat{A}\hat{B})f(x) = \hat{A}(\hat{B}f(x))$$

In multiplication, the order of the operators matters. In general, $\hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$. For example, consider the operators $\hat{x}$ and $\hat{p}$. If we take the product $\hat{x}\hat{p}$ and operate on f(x), we get

$$g(x) = \hat{x}\hat{p}f(x) = -i\hbar x \frac{\partial f(x)}{\partial x}$$

If however, we take the product $\hat{p}\hat{x}$, we get

$$g(x) = \hat{p}\hat{x}f(x) = -i\hbar \frac{\partial}{\partial x}(xf(x)) = -i\hbar(f(x) + x\frac{\partial f(x)}{\partial x}).$$

If $\hat{A}\hat{B}f(x) = \hat{B}\hat{A}f(x)$ then the operators are said to **commute**. The significance of this is that **if two operators commute**, then their observables can be measured simultaneously with infinite precision, i.e., **the uncertainty principle does not apply to that pair of variables**. **If they do not commute, then the uncertainty principle does apply**. For example, we have just shown that $\hat{x}$ and $\hat{p}$ don't commute, which means that the uncertainty principle applies to position and momentum. A common function which is used to evaluate whether two operators commute is the commutator, $[\hat{A}, \hat{B}]$, which is defined by the relation,

$$[\hat{A}, \hat{B}]f(x) = (\hat{A}\hat{B} - \hat{B}\hat{A})f(x).$$

If the commutator is zero, then the operators commute and the uncertainty principle doesn't apply. If however, $[\hat{A}, \hat{B}] = \frac{\hbar}{i}$, then the uncertainty principle applies. Note that in most

cases, you cannot properly evaluate commutation unless the operators are operating on a function.

In addition to the operators I've already shown you, we will determine other operators as we need them.

Once we obtain the operator for an observable, another postulate says that **if the wavefunction ψ_i of the system is an eigenfunction of an operator, then the only measured value of the observable will be the eigenvalue corresponding to this eigenfunction.** Let me repeat this, because it is very important. If the wavefunction ψ_i that defines the state of a system is an eigenfunction of some operator, then the only measured value of the observable associated with that operator will be the eigenvalue a_i associated with that eigenfunction.

However, if the wavefunction of the system, which we also call the state of the system, is **not** an eigenfunction of the operator, then each measurement made on the system will still be **one** of the eigenvalues of the operator. We are just unable to predict which of the eigenvalues it will be. However, later we'll learn how to calculate the **probability** that a given eigenvalue will be observed.

Lecture 7

Let's see how what we've talked about so far works by applying it to a pair of simple systems. The simplest problems in quantum mechanics are the free particle and the particle in a one-dimensional box. A **free particle** is one that can move unconstrained through space, with no potential impeding its motion. In other words, **for the free particle moving in one dimension, V(x) = 0**. Thus the Schrödinger equation for the free particle is

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

which we can rewrite as

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi,$$

where k $= (\frac{2mE}{\hbar^2})^{1/2}$, and is called the wavevector of the particle. The most general solution to this equation is

$$\psi(x) = (A\cos kx + B\sin kx).$$

We can see that this satisfies the Schrödinger equation by plugging this value of ψ into our equation. When we insert our solution into the Schrödinger equation, we get

$$\frac{\partial^2}{\partial x^2}(A\cos kx + B\sin kx) = -k^2(A\cos kx + B\sin kx) = -k^2\psi,$$

just as our equation requires.

There are two main conclusions we can draw from this result. The first we can draw by calculating $\psi^*\psi dx$, the probability. This shows that the probability of finding a particle is the same anywhere along the x axis, just as we would expect for a particle

unconstrained by any potential energy. The second is that the energy can take on any value.

We can see this since solving for the energy in terms of k yields $E = \dfrac{\hbar^2 k^2}{2m}$ and since the

solution to our Schrödinger equation contains no integers, it places no restriction on the

value of k. In other words, **the energy of a free particle is not quantized**.

The **particle in a one-dimensional box** is very similar to the free particle. In this

system a particle of mass m is constrained to move within some length a along the x axis.

For this problem, the potential energy function is given by

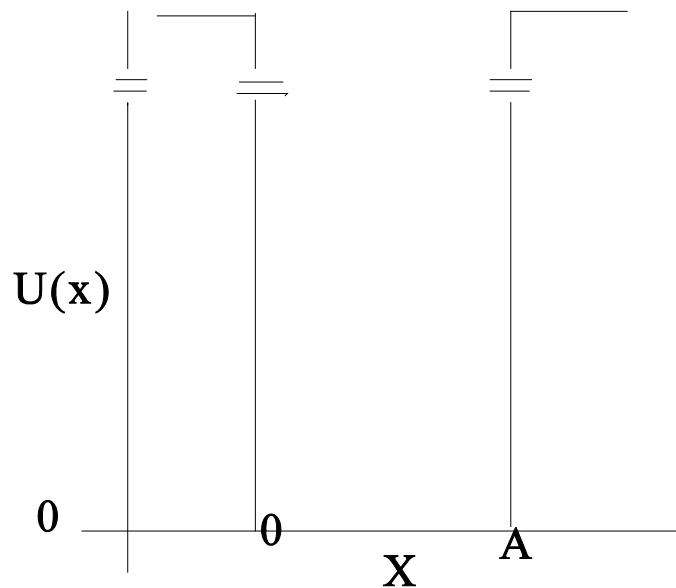$$V(x) = 0, \quad 0 \le x \le a$$

$$V(x) = \infty, \quad x < 0, x > a.$$

U(x)

0

0

X

A

Figure 1: Potential Energy V(x) For Particle in a Box

In other words, because it is confined by a potential barrier of infinite height, the particle

can only move between zero and a. It is similar to the free particle because between 0 and

A the potential is zero. It differs because in this problem there are two boundaries defining

regions where it is impossible for the particle to be, since the potential is infinity. We want

to determine $\psi(x)$ for all three of the regions of space defined by this potential. For x > a and x < 0 this is trivial. Since $V(x) = \infty$ in these regions it is impossible for the particle to be there, and therefore the probability amplitude, $\psi(x)$, must be zero everywhere in these regions.

In the region $0 \leq x \leq a$, $V(x) = 0$ and the Schrödinger equation is

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

which just as before can be rewritten as

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi$$

where $k = (\frac{2mE}{\hbar^2})^{1/2}$, just as it was for the free particle. Once again the general solution to this equation is

$$\psi(x) = A\cos kx + B\sin kx.$$

But we haven't yet accounted for the fact that our particle can only be found between 0 and a. Remember that $\psi(x)$ must be continuous for all values of x. The region where we have to pay particular attention to this is at the boundary of the region in which the particle moves. At x = 0, ψ must be equal to zero, since $\psi = 0$ for x<0. Similarly at x = a, ψ must also equal zero, since $\psi = 0$ for all x > a. We call these constraints on the value of ψ at the boundary of our potential well **boundary values**.

These **boundary values place constraints on our solution**. We see the first of these by setting x = 0 and setting $\psi = 0$ in compliance with our first boundary value. This gives us

$$\psi(0) = 0 = A\cos 0 + B\sin 0 = A.$$

Therefore A = 0 and our wavefunction simplifies to

$$\psi(x) = B \sin kx.$$

We see our second constraint by applying our second boundary condition, setting x = a and

ψ = 0. This gives us

$$\psi(a) = 0 = B \sin ka$$

This will only equal zero when B = 0 or when ka = π, 2π, 3π,..., nπ,...., where n is an

integer. Since B=0 yields zero for the whole wavefunction, this is not an interesting

solution, since this means that the probability is zero that the particle will be described by

the wavefunction. For this reason we will focus on our second solution. For this we can

write

$$k = \frac{n\pi}{a}.$$

and our wavefunction becomes

$$\psi(x) = B \sin \frac{n\pi x}{a}$$

If we normalize this as before, we get finally,

$$\psi(x) = (\frac{2}{a})^{1/2} \sin \frac{n\pi x}{a}$$

Note that the requirement $k = \frac{n\pi}{a}$ leads to the quantization of the energy of the

particle in a box, since

$$k = (\frac{2mE}{\hbar^2})^{1/2} = \frac{n\pi}{a}$$

Solving this equation for E yields

$$E = \frac{n^2 h^2}{8ma^2},$$

which is quantized because of the presence of the integers in the equation.

Notice that the general solutions to the Schrödinger equation for the free particle and the particle in a box are identical. The only difference between the two problems is the presence of the boundaries that constrain the movement of the particle in the particle in a box. We will find that **every time a boundary constrains the motion of a particle, the energy of that particle will be quantized**. In the absence of these constraints the particle can take on any energy.

What are some of the physical consequences of these results? First, notice that there is a minimum energy for the particle in a box. The lowest energy is when n= 1 and is equal to $E_1 = \frac{h^2}{8ma^2}$. This minimum energy is called the zero point energy of the system. Why can't n = 0? The reason is that substituting n=0 in our equation for the wavefunction of the particle in a box yields ψ=0 for all values of x. Since the probability of finding a particle in a given position is given by $\psi*(x)\psi(x)dx$, this means that the probability of finding a particle in a state with n=0 is identically zero.

There is an interesting corollary to this. If n was 0 the energy would equal zero, the particle would be motionless and would violate the uncertainty principle, since in order for the particle to be motionless, it's position uncertainty would have to be infinite, and therefore the particle could not be confined to the box. In other words, the uncertainty principle forbids that any bound system be entirely motionless, i.e., not only thermodynamics but quantum mechanics forbids any system from reaching a temperature of absolute zero.

As the quantum number n increases, the energy of the particle increases, with

$$E_2 = \frac{4h^2}{8ma^2}, \; E_3 = \frac{9h^2}{8ma^2}. \text{ etc.}$$

Now that we've looked at the eigenvalues for the particle in a box, let's look at the eigenfunctions. If we plot the wavefunctions for n = 1, n = 2, etc., we see that they take on the appearance of standing waves. Notice that n=1 contains 1/2 of a wave, n=2 contains a full wave, n = 3 contains 3/2 wave, and in general level n will contain n/2 waves, i.e., each level contains an integral number of half waves. If we look at the probability density $\psi^*\psi$ for each of these levels, we find that for n = 1 the maximum probability is in the center of the box, at $\frac{a}{2}$. For n=2, there are two maxima, at $\frac{a}{4}$ and $\frac{3a}{4}$. As n increases, the probability density spreads out more and more, until at high n, the distribution is completely even, which is what we would expect classically. This is an important result. In general, a quantized system will approach the behavior predicted by classical mechanics (the classical limit) when the quantum numbers become very large. This is called the **correspondence principle**, due to Neils Bohr.

Notice that in our probability distribution there are points, besides the fixed points at x = a and x = 0, where the probability density is zero. These points are called **nodes**. In many problems of interest to us, including the harmonic oscillator, the particle in a one and three dimensional box, the rigid rotator and the hydrogen atom, **the higher the number of nodes in a state the higher the energy of that state**. For the particle in a box, the number of nodes is related to n by

nodes = n - 1.

The particle in a box may seem like an artificial problem with no applications to real world systems, but it has in fact been applied to the spectroscopy of linear conjugated molecules. This is because the particle in a box is a fair approximation for the energies of π electrons in linear conjugated systems. Consider, for example, butadiene. For the sake of simplicity, we'll assume that the π-electrons move in a straight line whose length, a, is equal to the sum of the C-C bond lengths plus the van der Waals radii of the two terminal carbon atoms.
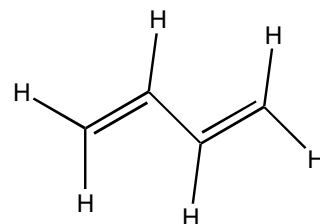
$$a = 2\ell_{C=C} + \ell_{C-C} + 2r_{vdW} \text{ (C)}$$

$$= 2 \times 135 \text{ pm} + 154 \text{ pm} + 2 \times 77 \text{ pm} = 578 \text{ pm} = 5.78 \times 10^{-10} \text{ m}.$$

Thus we will model the electrons as moving in a 5.78×10^{-10} m box. According to the solution for the particle in a one dimensional box,

$$E_n = \frac{n^2 h^2}{8ma^2},$$

where in this case, as we have just shown, a, the length of the box, is equal to 5.78×10^{-10} m. The Pauli exclusion principle, which we will discuss in detail later, tells us that there can only be two electrons for each quantum number n. Butadiene has four π electrons. We place two in the lowest state of our particle in a box, n = 1, and the final two in n = 2. Thus for butadiene, the highest occupied molecular orbital is n = 2, i.e., HOMO = 2. The lowest unoccupied molecular orbital, LUMO, is n = 3. The electronic absorption should occur at

the energy necessary to promote an electron from the HOMO to the LUMO, i.e., from n =

2 to n= 3. The energy of this transition is

$$\Delta E(3 \leftarrow 2) = \frac{9h^2}{8ma^2} - \frac{4h^2}{8ma^2} = 9.02x10^{-19} J$$

This corresponds to an absorption at 220 nm. Butadiene has an absorption at 217 nm, so

we see that despite its simplicity, the particle in a box is a fairly good model for the

ultraviolet spectra of simple conjugated models.

Lecture 8

At this point, we've seen our first example of how to solve the Schrödinger equation. We've seen how to use the eigenfunctions we've obtained to describe the probability of finding the system in various positions. We've also seen how to extract information from our eigenfunctions – we determined the energy by operating on our eigenfunctions with the Hamiltonian (total energy) operator.

However, we still need to learn more about the mechanics of quantum mechanics – for example, we don't yet know how to extract information from a wavefunction when it is not an eigenfunction, i.e., not a solution of an eigenvalue equation. We already have made a couple of statements about these types of wavefunctions, first that even though they are not eigenfunctions of our operators, we'll still always observe only eigenvalues of the operator but that we can't predict which one, and second, that we can predict the probability of observing a given eigenfunction. In order to understand why these statements are true, we'll have to learn something about the **mathematical properties of eigenfunctions**.

We've already stated that to be consistent with their interpretation as probability amplitudes, eigenfunctions must be normalized. This condition is usually written as

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j d\tau = 1 \ \ if \ i = j$$

At this point, I'd like to show you another form for writing this equation, the so-called Dirac Bra-Ket notation. Dirac chose to indicate the equation above as follows:

$$\langle \psi_i | \psi_j \rangle = 1 \ if \ i = j \,.$$

This equation means the same as the integral equation above. I am introducing it because this notation appears frequently in textbooks and the literature, and because it is a notation that easily bridges the Schrodinger and Heisenberg formulations of Quantum Mechanics.

In this equation, it is understood that the term on the left $\langle \psi_i |$, called a bra, represents the complex conjugate of ψ_i in the integral, while the term on the right, $| \psi_j \rangle$ called a ket, represents the second wavefunction and the rest of the integral. If ψ_i is an eigenfunction, then $\langle \psi_i |$ is called an eigenbra, and if ψ_j is an eigenfunction then $| \psi_j \rangle$ is called an eigenket. (Dirac chose Bra and Ket as the names for these symbols because in his notation the wavefunctions are surrounded by a bracket, and Bra and Ket are the two halves of bracket (if you spell poorly.) This clearly tells us something about how Dirac's mind worked, but I'm not sure what.

Another very important property of a set of eigenfunctions is that the product of two different eigenfunctions of the same operator integrated over all space is zero, i.e.,

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, d\tau = 0 \; if \; i \neq j \, ,$$

or in bra-ket notation

$$\langle \psi_i | \psi_j \rangle = 0 \; if \; i \neq j$$

When two wavefunctions satisfy this equation they are called **orthogonal wavefunctions**. So in other words if we generate a set of eigenfunctions by solving the Schrödinger equation, any two of these functions will be orthogonal. One interpretation of orthogonality is that each solution ψ_i occupies a unique axis, just as the x, y and z axes (which are orthogonal in 3-space) occupy unique portions of space. Note that this is true only in Hilbert space, an infinite dimensional space which is useful for many quantum mechanical manipulations.

Our two statements on orthogonality and normalization are usually represented by a single equation,

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j d\tau = \delta_{ij}$$

or

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

where δ_{ij} is called the **Kronecker delta function** which is defined by

$$\delta_{ij} = 0, \ i \neq j$$

$$\delta_{ij} = 1, \ i = j.$$

The members of sets of functions that are both orthogonal and normalized are called **orthonormal functions**.

It turns out that all discrete solutions to the Schrödinger equation are complete orthonormal sets of functions. A complete set is one where any function of a member of the set results in a function which is still a member of the set. **Complete orthonormal sets of functions are important because any arbitrary function $\psi(x)$ can be expressed as a linear combination of members of a complete orthonormal set of functions.** Thus any arbitrary wavefunction $\psi(x)$ can be expressed as a linear combination of eigenfunctions, $\psi_i(x)$. In other words,

$$\psi(x) = c_1 \psi_1(x) + c_2 \psi_2(x) + c_3 \psi_3(x) + ...$$

where $\psi(x)$ is any arbitrary wavefunction, the c_i's are constants, and the $\psi_i(x)$ are eigenfunctions of some operator. This rule, that any arbitrary wavefunction can be expressed as a linear combination of eigenfunctions, is sometimes referred to as the **superposition principle**. Since the functions that are being superposed have wave characteristics, the superposition principle opens up the possibility of constructive and destructive interference between wavefunctions.

This explains why we observe only eigenvalues even when our wavefunction $\psi(x)$ is not itself an eigenfunction. **Since any wavefunction that is not an eigenfunction is a linear combination of eigenfunctions, we are observing the eigenvalue of one of the eigenfunctions that make up our wavefunction. The probability of observing one of these eigenvalues is equal to the square of its coefficient, c_i^2.** T his implies that the sum of the squares of the coefficients must be one, i.e.,

$$\sum_i c_i^2 = 1.$$

Sometimes two eigenfunctions will have the same energy. In this case we say that the eigenfunctions are **degenerate**. One property of degenerate eigenfunctions is that **all linear combinations of degenerate eigenfunctions will also be eigenfunctions**. This is not true for nondegenerate eigenfunctions and all linear combinations of nondegenerate eigenfunctions will not be eigenfunctions.

Note that while the solutions we have obtained for the particle in a box are eigenfunctions of the Hamiltonian operator they are not eigenfunctions of the position operator $\hat{X}$. If this was so, $\hat{X}\psi(x) = x\psi(x)$ would equal a constant times $\psi(x)$, which is not the case. According to our postulates, if we have a state $\psi(x)$ which is an eigenfunction of the Hamiltonian but NOT an eigenfunction of the operator $\hat{X}$, we will obtain an eigenvalue of some eigenfunction of the operator $\hat{X}$ when we measure x, but we won't be able to predict which one. Repeated measurement of x will yield the probability densities we have calculated.

Even though we cannot predict the value of a given measurement when a wavefunction is not an eigenfunction of the operator in question, we can always predict the average value of the measurement. For this we need another postulate.

To introduce this postulate, we'll begin with a **review of averages**. Most of us are introduced to averages of what are called **discrete distributions**. The numbers you obtain by rolling a die are a discrete distribution, with the integers 1-6 the only possible results, and no intervening numbers possible. Discrete distributions are intrinsically discontinuous. In this case, the procedure for taking an average is simple. If you roll the die 5 times, you add the five numbers, divide by 5 and you have the average. For example if five rolls got you 1,3,2,4,3, your average is (1+3+2+4+3)/5 = 2.6. In general the average of N measurements of some observable F is given by

$$\langle F \rangle = \frac{\sum_1^N F_n}{N},$$

where the brackets indicate an average value. An alternative way of calculating the average for a discrete distribution is with the equation

$$\langle F \rangle = \sum_{f=1}^{N} p_f F_f$$

where p_f is the probability that the result F_f is observed. In our example above, the probability of observing 1,2, and 4 was 1 in 5 or .2, while the probability of observing 3 was 2 in 5 or .4, and the probability of observing 5 and 6 was zero. Our average is 1 x .2 +

2 x .2 + 3 x .4 + 4 x .2 + 5 x 0 + 6 x 0 = 2.6. The set of probabilities, $\{p_f\}$, is called a **discrete probability distribution**.

If our measurements can vary continuously, as would be the case for the measurement of a series of lengths, the average is calculated using a **continuous probability distribution** in place of the discrete probability distribution. If our continuous probability distribution is given by f(x), then the average of some variable x is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} xf(x)dx$$

This fits nicely into our quantum mechanical formulation, since **$\psi^*(x)\psi(x)dx$ is a continuous probability distribution**. However, there's a bit of a twist in quantum mechanics. A postulate of quantum mechanics says that **the average of a quantum mechanical observable A, is given by**

$$\langle a \rangle = \int_{-\infty}^{\infty} \psi^*(x)\hat{A}\psi(x)dx$$

or in bra-ket notation

$$\langle a \rangle = \langle \psi(x) | \hat{A} | \psi(x) \rangle.$$

Note that this equation does two things. The operator operating on ψ extracts the value or values of A that can be observed, and then the product with ψ^* gives us our average. Note that if $\psi(x)$ is an eigenfunction of $\hat{A}$, then <a> is simply the eigenvalue of $\hat{A}$, a_n. LET'S PROVE THIS CLAIM TOGETHER. NOW LET'S LOOK AT A SIMPLE LINEAR COMBINATION OF EIGENFUNCTIONS, $\psi = c_1\psi_1(x) + c_2\psi_2(x)$ AND SEE WHAT ITS AVERAGE IS.

Let's do a quick example and calculate the average position for the particle in a box. We'll make this a bit fancy and rather than calculate the average for a given state, we'll calculate a formula so we can see what the average is for any value of n. Before I

actually calculate the average, let's look at the probability density for a few states. [DRAW] CAN ANYONE PREDICT WHAT THE AVERAGE POSITION WILL BE? [a/2] The average is in the middle of our range of possible x values because our potential function is symmetric about the range of x. In general we will find that **any time we have a symmetric potential function our probability density will be symmetric as well.** The wavefunction for the particle in a box is

$$\psi_n = (\frac{2}{a})^{1/2} \sin \frac{n\pi x}{a}$$

Therefore the average of x over the range 0 to a is given by

$$\langle x \rangle = \int_0^a \psi^*(x) \hat{X} \psi^*(x) dx$$

$$= \int_0^a (\frac{2}{a})^{1/2} \sin \frac{n\pi x}{a} x (\frac{2}{a})^{1/2} \sin \frac{n\pi x}{a} dx$$

$$= \frac{2}{a} \int_0^a x \sin^2 \frac{n\pi x}{a} dx$$

This integral, while difficult, can be found in any standard table of integrals and yields

$$\langle x \rangle = \frac{2}{a}(\frac{a^2}{4}) = \frac{a}{2}$$

Note that this calculation yields the same result as our qualitative prediction of the probability density, that the average position is the same for all states of the particle in a box.

In addition to being able to calculate the average of an observable quantity, it is useful to know how widely a measurement is spread around the average. A useful measurement of this is the variance, σ_x^2. The variance is the square of a function that you

are all familiar with, the standard deviation, σ_x. Because of the manner in which we calculate quantum mechanical averages, in quantum mechanics the variance is most easily calculated by using the formula

$$\sigma_x^2 = <x^2> - <x>^2$$

Before we go ahead and calculate the spread, let's go back and look at our probability density for the particle in a box. WHAT IS THE TENDENCY IN THE SPREAD OF THE DISTRIBUTION AS WE GO UP IN ENERGY? In order to calculate the variance we need to be able to calculate $<x^2>$. WHAT IS THE FORMULA FOR THE AVERAGE OF x^2? So for the particle in a box,

$$\left\langle x^2 \right\rangle = \int_0^a (\frac{2}{a})^{1/2} \sin\frac{n\pi x}{a} x^2 (\frac{2}{a})^{1/2} \sin\frac{n\pi x}{a} dx = \frac{2}{a}\int_0^a x^2 \sin^2\frac{n\pi x}{a} dx$$

Of course, we look this up in our handy table of integrals to find that

$$\left\langle x^2 \right\rangle = (\frac{a}{2\pi n})^2 (\frac{4\pi^2 n^2}{3} - 2)$$

Since we now know $<x>$ and $<x^2>$, we can calculate the variance,

$$\sigma_x^2 = \left\langle x^2 \right\rangle - \left\langle x \right\rangle^2 = (\frac{a}{2\pi n})^2 (\frac{\pi^2 n^2}{3} - 2)$$

If you plot the variance as a function of n you will find that this formula matches our intuition and that as n increases the probability distribution gets wider. AS A HOMEWORK ASSIGNMENT, CALCULATE THIS VARIANCE FOR N = 1 TO 10, FOR A BOX WITH A = 1.00 NM. So we now have two tools to help us understand the nature of a probability distribution, the average or expectation value and the variance. One way that the variance is used is as a measure of the uncertainty of an observable. The larger the variance, the larger the uncertainty.

Lecture 9

Many of the problems that are of the greatest interest to chemists are **multidimensional**. For example, the rigid rotor, the simplest model of a rotating molecule, is two dimensional, while the hydrogen atom is three dimensional, and the vibration of most polyatomic molecules turns out to be 3N-6 dimensional, where N is the number of atoms in the molecule. While each of these problems has its own unique features, all of them have certain common features. We can see what these are by studying the simplest three-dimensional problem, the **particle in a three-dimensional box**.

In this problem the particle is contained in a box with sides of length a, b, and c. Outside of the box the potential is ∞. We write this as the set of conditions

$$V = 0 , \; 0 \le x \le a; \; 0 \le y \le b; \; 0 \le z \le c$$

$$V = \infty, \text{ elsewhere.}$$

The Schrödinger equation for a single particle moving in three dimensions is

$$\hat{H}\psi(x,y,z) = E\psi(x,y,z)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z),$$

and where ∇^2 is called the Laplacian, which is the dot product of two gradients, where the gradient ∇ is defined as

$$\nabla = \vec{i}\,\frac{\partial}{\partial x} + \vec{j}\,\frac{\partial}{\partial y} + \vec{k}\,\frac{\partial}{\partial z},$$

and is a vector quantity where $\vec{i}$, $\vec{j}$, and $\vec{k}$ are unit vectors along the x, y and z axes respectively. The dot product of the gradient with itself, the Laplacian, is a scalar quantity and is equal to

$$\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

So we see that two differences in our three dimensional case are that the **wavefunctions will be functions of x, y, and z**, and the **partials are taken not just with respect to x, but with respect to y and z** as well. For cases where the potential is not zero, the potential will be a function of up to three variables as well. For a wavefunction in three dimensions, x, y, and z, the **probability density is** $\psi^*(x,y,z)\psi(x,y,z)$, the probability that a particle will be found in an infinitesimal volume near x,y,z is given by

$$prob\{x, x+dx; y, y+dy, z, z+dz\} = \psi^*(x,y,z)\psi(x,y,z)dxdydz,$$

while the probability that we will find the particle in the finite volume bounded by x_1, x_2, y_1, y_2, z_1 and z_2, is given by the triple integral,

$$prob\{x_1, x_2; y_1, y_2; z_1, z_2\} = \int_{x_1}^{x_2} \int_{y_1}^{y_2} \int_{z_1}^{z_2} \psi^*(x,y,z)\psi(x,y,z)dxdydz$$

Since this integral, as was the case for the one-dimensional problem, is also a probability, we have the same requirements as before for normalizability, single valuedness and continuity.

A **multiple integral** is sort of a partial derivative in reverse. What you do is choose one variable to integrate at a time and hold the others constant. Then you choose the next and so on. For example, consider the integral of the simple function $xy + yz + zx$. The full triple integral is

$$\iint\limits_{x\ y\ z}\int (xy+yz+zx)dxdydz$$

Let's do the integral with respect to x first, treating y and z as constants.

$$\int_x\int_y\int_z xy+yz+zxdxdydz = \int_y\int_z(\frac{x^2y}{2}+xyz+\frac{zx^2}{2}+c_1)dydz$$

Now we integrate with respect to y.

$$\iint\limits_{x\ y\ z}\int (xy+yz+zx)dxdydz = \int_z(\frac{x^2y^2}{4}+\frac{xy^2z}{2}+\frac{zx^2y}{2}+c_1y+c_2)dz$$

Finally, we integrate with respect to z.

$$\iint\limits_{x\ y\ z}\int xy+yz+zxdxdydz = \frac{x^2y^2z}{4}+\frac{xy^2z^2}{4}+\frac{z^2x^2y}{4}+c_1yz+c_2z+c_3$$

Note that the order of the integrations is not important. When I was taught how to do this we generally chose to do the easiest integral first.

Now let's return from our brief digression on multiple integrals and return to our consideration of the particle in a three dimensional box. SINCE V(X,Y,Z) = 0 INSIDE THE BOX, WHAT WILL THE SCHRÖDINGER EQUATION FOR THIS PROBLEM BE? [$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\psi(x,y,z) = E\psi(x,y,z)$] The usual method for solving multidimensional problems of this sort is called **separation of variables**. What we do is **assume that ψ(x,y,z) can be written as the product of three functions of one variable, i.e.,**

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

This assumption is valid as long as you can write your Hamiltonian as the sum of three Hamiltonians of a single variable only. In the case of the particle in a three dimensional box,

$$\hat{H} = -\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} = \hat{H}_1(x) + \hat{H}_2(y) + \hat{H}_3(z)$$

Since we've broken down our Hamiltonian into three Hamiltonians of one variable each, separation of variables is valid for this problem. The effect of separation of variables is to break our problem down into three one-dimensional problems,

$$\hat{H}_x X(x) = E_x X(x)$$

$$\hat{H}_y Y(y) = E_y Y(y)$$

$$\hat{H}_z Z(z) = E_z Z(z)$$

where the total energy $E = E_x + E_y + E_z$. Since each of these one dimensional problems is exactly the same as the one dimensional particle in a box, we can immediately write down solutions for X(x), Y(y) and Z(z).

$$X(x) = (\frac{2}{a})^{1/2} \sin\frac{n_x \pi x}{a}, E_x = \frac{n_x^2 h^2}{8ma^2}$$

$$Y(y) = (\frac{2}{b})^{1/2} \sin\frac{n_y \pi y}{b}, E_y = \frac{n_y^2 h^2}{8mb^2}$$

$$Z(z) = (\frac{2}{c})^{1/2} \sin\frac{n_z \pi z}{c}, E_z = \frac{n_z^2 h^2}{8mc^2}$$

This means that

$$\psi(x, y, z) = X(x)Y(y)Z(z) = (\frac{8}{abc})^{1/2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}$$

and

$$E_{n_x, n_y, n_z} = E_x + E_y + E_z = \frac{h^2}{8m}(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2})$$

Notice that in a particle in a one dimensional box, the energy and the wavefunction depend on only one quantum number, n_x, while for a three dimensional particle in a box, the energy depends on three quantum numbers, n_x, n_y, and n_z. Therefore, the number of quantum numbers we need to describe a system increases as the number of dimensions increases.

Suppose that a> b> c. Then if we make a diagram of energy versus quantum number, the lowest energy is with all three quantum numbers, n_x, n_y, and n_z equal to one.

We symbolize this state as ψ_{111} and its energy as E_{111}. $E_{111} = \dfrac{h^2}{8m}(\dfrac{1}{a^2} + \dfrac{1}{b^2} + \dfrac{1}{c^2})$. The next

level is $E_{211} = \dfrac{h^2}{8m}(\dfrac{4}{a^2} + \dfrac{1}{b^2} + \dfrac{1}{c^2})$. The next is $E_{121} = \dfrac{h^2}{8m}(\dfrac{1}{a^2} + \dfrac{4}{b^2} + \dfrac{1}{c^2})$. and so on.

The energy level diagram takes on a different appearance if our box is cubic, i.e., if a = b = c. Then our energy equation becomes

$$E = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$$

Our lowest energy level is still $E_{111} = \dfrac{3h^2}{8ma^2}$. Our next lowest level is

$E_{211} = \dfrac{h^2}{8ma^2}(4 + 1 + 1) = \dfrac{6h^2}{8ma^2}$. But notice that E_{121} and E_{112} both have this same energy,

$\dfrac{6h^2}{8ma^2}$, as well. Each of these energy states corresponds to a different wavefunction, i.e.,

$$\psi_{121} = (\frac{8}{a^3})^{1/2} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi z}{a},$$

while

$$\psi_{211} = (\frac{8}{a^3})^{1/2} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a},$$

yet their energies are the same. When two or more different wavefunctions have the same energy, we say that they are **degenerate**. **Degenerate states are always due to some symmetry in the system**. For example, in this case, when a=b=c, the system has degenerate states. If a = b ≠ c, there are also degenerate states because as in our first case there is a level of symmetry. You can see this because for this case

$$E_{n_x n_y n_z} = \frac{h^2}{8m}(\frac{n_x^2 + n_y^2}{a^2} + \frac{n_z^2}{c^2}),$$

which means that

$$E_{211} = E_{121} = \frac{h^2}{8m}(\frac{5}{a^2} + \frac{1}{c^2}) \text{ while } E_{112} = \frac{h^2}{8m}(\frac{2}{a^2} + \frac{4}{c^2}).$$

However, for the case where a ≠ b ≠ c, and there is no other symmetry, there are no degenerate states. Degenerate states are at the core of several phenomena, the most familiar of which is NMR.

To summarize: If **you have a Hamiltonian, $\hat{H}$, which can be written as the sum of component Hamiltonians of one variable, $\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$, then the solution, ψ(x,y,z), will be the product of three one dimensional wavefunctions, $\psi(x,y,z) = X(x)Y(y)Z(z)$, and its energy will be the sum of the eigenvalues of the one dimensional eigenvalue equations, $E = E_x + E_y + E_z$.**