

Chemistry 7000

Introductory Quantum Chemistry

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No set office hours - but come by to ask questions anytime. If I am around, I'll be happy to answer your questions.

Before beginning quantum mechanics, let's first think about classical mechanics, which was first expounded by Sir Isaac Newton (1643-1727) in Principia (1687, in Latin). Classical mechanics deals with the motion of macroscopic bodies, and is a tremendously successful theory. It explains all observations regarding macroscopic objects except for objects moving very fast (where special relativity becomes important) or objects subjected to large gravitational fields (where general relativity becomes important).

The central relationship in classical mechanics is Newton's equation of motion:

$$F = ma, \text{ or } F = m \frac{d^2x}{dt^2}$$

This equation states that the acceleration on an object is completely determined by the forces acting on the object. Furthermore, we can integrate the equation twice to obtain the trajectory of the object, as

$$x(t) = x(0) + \left(\frac{dx}{dt}\right)_0 t + \int_0^t dt' \int_0^{t'} dt'' \frac{F(t'')}{m}$$

Thus, given knowledge of the initial position ( $x(0)$ ), initial velocity ( $\left(\frac{dx}{dt}\right)_0$ ), and forces ( $F(t)$ ) acting on the particle, it is possible to solve for the motion of the particle into the indefinite future.

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Classical mechanics is in our bones. We live it every day, when we drive a car, toss a ball, or even lift a pencil. We understand it instinctively, and it makes sense to us.

Quantum mechanics is a step more abstract. It applies to the microscopic world, where we have no direct experience, and it seems strange to us. The simple idea of a trajectory of a particle,  $x(t)$ , no longer exists in such a simple form when we move to quantum mechanics. Nevertheless, quantum mechanics provides a remarkably accurate theory to explain the properties and behavior of small objects. Further classical mechanics develops naturally as the limiting form of quantum mechanics in the limit of large quantum numbers, or high energies.

In quantum mechanics the central new concept that must be introduced is that of the wavefunction,  $\Psi$ , which determines everything that can be measured about the system.

### Postulate I: (Schrödinger, 1926)

(a) The state of a system composed of  $N$  particles is described as fully as possible by its wavefunction,  $\Psi(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N, t)$ , which contains all information about the system.

[Postulate 4 in book] (b) The quantity  $|\Psi|^2 dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \dots dx_N dy_N dz_N$  provides the probability of finding particle 1 in a small volume  $dx_1 dy_1 dz_1$  about the point  $(x_1, y_1, z_1)$  while simultaneously finding particle 2 in the small volume  $dx_2 dy_2 dz_2$  about  $(x_2, y_2, z_2)$ , while simultaneously finding particles 3, 4, ...,  $N$  in their respective volumes, all at time  $t$ . [Born interpretation]

This interpretation of  $|\Psi|^2$  as a probability density is due to Max Born, and is called the Born interpretation.

As in classical mechanics, quantum mechanics has an equation of motion, which describes how the system evolves in time. In classical mechanics this is Newton's equation  $F=ma$ , or its equivalents. In quantum mechanics this equation is the time-dependent Schrödinger equation

$$\hat{H} \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

which for a particle moving in one-dimension is:

Postulate II: (Schrödinger, 1926)

The equation of motion for  $\Psi$  which determines the time evolution of  $\Psi$  and therefore the time evolution of all measurable properties is:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

where  $m$  = mass of particle,  $V(x)$  is the potential energy of the particle as a function of position,  $x$ ,  $i$  is the square root of  $-1$  (the imaginary number).  $\hbar$  is Planck's constant,  $h$  ( $6.626 \times 10^{-27}$  erg-sec) over  $2\pi$

Just as in classical mechanics this equation can be solved to obtain the wavefunction  $\Psi$  as a function of all future times if the forces in the system are completely known [in the form of the potential,  $V(x)$ ] and if the initial state of the system,  $\Psi(x, t=0)$  is completely known. The difference is that this equation is a bit more difficult to solve than Newton's equation, and one must then take the additional

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step of extracting the properties of interest from  $\Psi(x,t)$  once that is known.

Right about now you are no doubt wondering where these equations have come from. By baldly stating these as postulates, I have adopted a strategy that is justified by the fact that the results we obtain are in such excellent agreement with experiment. But, of course, these ideas were not just developed out of thin air. Instead, they developed naturally from the analogy between light and matter. By the 1920's light was very well understood as an electromagnetic wave, and at the same time the idea of the photon was developed. The intensity of electromagnetic radiation was given as the square of the electric field of the radiation, and it is the intensity of the radiation that is proportional to the number of photons passing through a given area per second. Thus,  $|E|^2$  is proportional to the probability of finding a photon in a particular location. This is very similar to the Born interpretation of the wavefunction.

Likewise a strong analogy exists between the propagation of light as waves, and the time-dependent Schrödinger equation, and Atkins and Friedman use this analogy to argue for the plausibility of the Schrödinger equation on pages 34-38. I will not have time to work through this with you in this course, since I have too much material to cover. This contains some very useful concepts, however, and I recommend this section for you to read. It is interesting.

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Because  $|\Psi|^2$  is to be interpreted as a probability density, we must place certain restrictions on  $\Psi$ :

(1) Every particle must be somewhere in space.

$$\therefore \int_{\text{all space}} |\Psi|^2 d\tau = 1 \quad [\Psi \text{ must be normalized}]$$

Note: If  $|\Psi|^2$  is sharply peaked, the particle is located in a narrowly defined region of space, and it really looks particle-like.

If  $|\Psi|^2$  is broad and diffuse, it looks like a wave rather than a particle is present.

(2)  $\Psi$  is not itself observable; only  $|\Psi|^2$  [defined as  $\Psi^* \Psi$ , where  $\Psi^*$  is the complex conjugate of  $\Psi$ , obtained by replacing  $i$  with  $-i$  everywhere it appears] is related to observable quantities.

(3) For  $\Psi$  to be a proper wavefunction, it must be single-valued and continuous.

NEXT: If all information that one can know about a system is contained in  $\Psi$ , how can we extract it?

ANSWER: Through the use of operators.

Postulate IIIA. Every observable dynamical quantity corresponds to a linear, Hermitian operator, which acts on the wavefunction to provide information pertinent to that observable.

A few definitions are needed here:

An operator is a rule for creating a new function from a given function. (In this course I will represent operators by placing a hat on them, to distinguish them from other quantities).

Examples:

$\hat{x}$  - multiplication by  $x$

$\frac{d}{dx}$  - differentiation with respect to  $x$

$\int_0^x dx$  - integration from 0 to  $x$

SQRT - taking the square root of the function.

An operator,  $\hat{A}$ , is linear if it obeys the two rules:

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

and  $\hat{A}(cf(x)) = c\hat{A}f(x)$ , where  $c$  is a constant.

Note: These rules must be obeyed for all choices of the functions  $f$  and  $g$ .

An operator  $\hat{A}$  is Hermitian if it satisfies the requirement:

$$\int_{\text{all space}} \psi_m^* \hat{A} \psi_n d\tau = \left[ \int_{\text{all space}} \psi_n^* \hat{A} \psi_m d\tau \right]^*$$

for all choices of  $\psi_n$  and  $\psi_m$  which are suitable candidates for a wavefunction (that is for all single-valued, continuous, and normalized [or normalizable] functions.)

Note: The definition that  $\hat{A}$  is Hermitian if  $\int \psi_m^* \hat{A} \psi_n d\tau = \left[ \int \psi_n^* \hat{A} \psi_m d\tau \right]^*$  is equivalent to this.

The use of linear Hermitian operators to represent observable quantities allows many useful theorems to be derived in quantum mechanics.

How do we obtain operators for specific observables? 7

### Postulate III B:

The operators for all dynamical quantities are constructed as combinations of the operators for position,  $\hat{x}$ , and its conjugate momentum,  $\hat{p}_x$ , according to the classical mechanical formulas.

Thus, in classical mechanics kinetic energy is given as

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\frac{p}{m}\right)^2 = \frac{p^2}{2m}$$

Therefore, the quantum-mechanical operator for kinetic energy is given by

$\hat{T} = \frac{\hat{p}^2}{2m}$ , where  $\hat{p}^2$  implies that the momentum operator acts twice in succession.

Postulate III C: The position and conjugate momentum operators  $\hat{x}$  and  $\hat{p}_x$  must satisfy the commutation relation:

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar, \quad \text{or} \quad [\hat{x}, \hat{p}_x] = i\hbar$$

where  $[\hat{x}, \hat{p}_x] = \hat{x}\hat{p}_x - \hat{p}_x\hat{x}$  is the commutator of  $\hat{x}$  and  $\hat{p}_x$ .

by which we mean that

$$\hat{x}\hat{p}_x\psi - \hat{p}_x\hat{x}\psi = i\hbar\psi \quad \text{for all possible}$$

choices of  $\psi$  while obey the requirements for an acceptable wave function. [This postulate is most appropriately credited to Heisenberg, who used in the development of "matrix mechanics."]

Note: This commutation relationship is only required for the each Cartesian coordinate and its conjugate momentum (i.e., momentum along that Cartesian coordinate). Different coordinate operators commute with one another. Different momentum operators commute with one another and position and momentum operators corresponding to different coordinates

also commute.

Thus, for example, for a particle moving in three dimensions,  $x, y,$  and  $z$ , we have three independent position operators,  $\hat{x}, \hat{y},$  and  $\hat{z}$ , and three independent momentum operators,  $\hat{p}_x, \hat{p}_y,$  and  $\hat{p}_z$ . Out of the set of six operators  $\{\hat{x}, \hat{y}, \hat{z}, \hat{p}_x, \hat{p}_y, \hat{p}_z\}$ , all combinations commute with one another except  $[\hat{x}, \hat{p}_x], [\hat{y}, \hat{p}_y],$  and  $[\hat{z}, \hat{p}_z]$ .

Postulate III C is of crucial importance to quantum mechanics, since it lies at the core of many of the puzzling aspects of quantum mechanics. For example this postulate is ultimately responsible for the famous Heisenberg uncertainty principle, as we shall see later.

Given that  $\hat{x}$  and  $\hat{p}_x$  must satisfy  $\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$  we have several choices for how we represent  $\hat{x}$  and  $\hat{p}_x$ :

Choice 1: The coordinate representation

Represent  $\psi$  as a function of  $x$  with multiplication by  $x$  as the  $\hat{x}$  operation.

With this choice,  $\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$  satisfies Postulate III C:

$$\begin{aligned} \text{Proof: } \hat{x}\hat{p}_x\psi - \hat{p}_x\hat{x}\psi &= x \frac{\hbar}{i} \frac{d\psi}{dx} - \frac{\hbar}{i} \frac{d(x\psi)}{dx} \\ &= \frac{\hbar}{i} \left( x \frac{d\psi}{dx} - \frac{d}{dx}(x\psi) \right) \\ &= \frac{\hbar}{i} \left( x \frac{d\psi}{dx} - \left[ \psi + x \frac{d\psi}{dx} \right] \right) \\ &= \frac{\hbar}{i} \left( x \frac{d\psi}{dx} - \psi - x \frac{d\psi}{dx} \right) \\ &= -\frac{\hbar}{i} \psi \left( \frac{i}{i} \right) = \frac{-\hbar i}{-i} \psi = i\hbar \psi \end{aligned}$$

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$$\therefore \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar, \text{ as required}$$

This, the coordinate representation, is by far the most commonly used choice. It is not the only choice, however.

Choice 2: Represent  $\Psi$  as a function of momentum,  $p$ , with multiplication by  $p$  as the  $\hat{p}$  operator. With this choice  $|\Psi(p)|^2 dp$  represents the probability of finding the particle with a momentum in the range between  $p$  and  $p+dp$ . With this choice the definition

$$\hat{x} = i\hbar \frac{d}{dp}$$

satisfies Postulate III c.

$$\begin{aligned} \text{Proof: } (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\Psi &= i\hbar \frac{d}{dp}(p\Psi) - p i\hbar \frac{d}{dp}\Psi \\ &= i\hbar \left( \frac{d}{dp}(p\Psi) - p \frac{d\Psi}{dp} \right) \\ &= i\hbar \left( \Psi + p \frac{d\Psi}{dp} - p \frac{d\Psi}{dp} \right) \\ &= i\hbar \Psi \end{aligned}$$

So  $\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$ , regardless of  $\Psi$ , as required.

This choice is called the momentum representation and is useful in solving certain problems, particularly when the potential,  $V(x)$  is simple.

We will not devote much attention to the momentum representation in this course.

Choice 3: The matrix representation.

Finally,  $\Psi$  may be represented as a vector with an infinite number of components, and which is transformed into other vectors by the operators  $\hat{x}$  and  $\hat{p}_x$ . Since matrices do not commute under the rules of matrix multiplication, it is then possible to construct matrices which represent  $\hat{x}$  and  $\hat{p}_x$ , and which act on the vector  $\Psi$  to generate a new vector. For these matrices to be valid descriptions of  $\hat{x}$  and  $\hat{p}_x$ , the matrices must act on the vector  $\Psi$  in such a way that Postulate III C is satisfied. This means that

$$\underline{\underline{x}} \underline{\underline{p}}_x - \underline{\underline{p}}_x \underline{\underline{x}} = i\hbar = \begin{pmatrix} i\hbar & 0 & 0 & 0 & \dots \\ 0 & i\hbar & 0 & 0 & \dots \\ 0 & 0 & i\hbar & 0 & \dots \\ 0 & 0 & 0 & i\hbar & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix},$$

where  $\underline{\underline{x}}$  and  $\underline{\underline{p}}_x$  are the matrices representing  $\hat{x}$  and  $\hat{p}_x$ , and  $\underline{\underline{x}} \underline{\underline{p}}_x$  indicates matrix multiplication.

We will not initially devote much attention to the matrix representation of quantum mechanics in this course, but we will return to it later.

### Postulate IV:

(a) If  $\psi$  is an eigenfunction of the operator  $\hat{A}$  with eigenvalue  $a$ , then a measurement of the property corresponding to  $\hat{A}$  will always give the value  $a$ , within the limits of the instrument, with absolute certainty.

Here I have introduced two new concepts: eigenfunction and eigenvalue. The function  $\psi$  is an eigenfunction of the operator  $\hat{A}$  if  $\hat{A}$  acts on  $\psi$  to return a multiple of  $\psi$ . The multiplicative factor that is returned is the eigenvalue.

Thus, if

$$\hat{A}\psi = a\psi \quad \text{we have an eigenvalue equation.}$$

Operator                      Eigenfunction                      Eigenvalue

Postulate IV (a) tells us that the only possible results of a measurement are the eigenvalues of the corresponding operator.

As an example of an eigenfunction, consider the momentum operator in the coordinate representation, given by  $\hat{p} = \frac{\hbar}{i} \frac{d}{dx}$ . This operator has an eigenvalue equation given by

$$\hat{p}\psi = p\psi, \quad \text{where } p \text{ is the eigenvalue.}$$

We may solve for the eigenfunctions and allowed eigenvalues by substituting the explicit form of  $\hat{p}$  to give:

$$\frac{\hbar}{i} \frac{d\psi}{dx} = p\psi.$$

This differential equation may now be solved for  $\psi$ :

$$\frac{\hbar}{i} \frac{d\psi}{dx} = p\psi$$

$$\frac{d\psi}{\psi} = \frac{ip}{\hbar} dx$$

$$\int \frac{d\psi}{\psi} = \int \frac{ip}{\hbar} dx = \frac{ip}{\hbar} \int dx$$

↑ All are constants

$$\ln \psi = \frac{ip}{\hbar} (x - C)$$

$$\psi(x) = \exp \left[ \frac{ipx}{\hbar} - \frac{ipC}{\hbar} \right]$$

$$= \exp \left[ \frac{ipx}{\hbar} \right] \exp \left[ -\frac{ipC}{\hbar} \right]$$

↑ All are constants

$$= C' \exp \left[ i \frac{px}{\hbar} \right]$$

$$\boxed{\psi(x) = C' e^{ipx/\hbar}}$$

This represents the wavefunction for a particle constrained to move along the  $x$  axis with a fixed and definite momentum,  $p$ . If  $p$  is positive, it is moving toward positive values of  $x$ ; if negative, it is moving toward negative values of  $x$ .

Ordinarily,  $C'$  would be fixed by requiring  $\psi$  to be normalized, but this cannot be done in this instance, because the particle can move over all of space. It is a free particle.

Postulate IV (b):

When  $\Psi$  is not an eigenfunction of  $\hat{A}$ , it can always be expanded as a linear combination of eigenfunctions of  $\hat{A}$ , as:

$\Psi(x) = \sum c_n \psi_n$ , where the  $\psi_n$  are eigenfunctions of  $\hat{A}$  with eigenvalues  $a_n$ :

$$\hat{A} \psi_n = a_n \psi_n$$

Under these conditions, the probability of making a measurement of the property  $A$  and getting the value  $a_n$  is given by  $|c_n|^2$ .

Note: Postulate IV (a) is a special case of this version of the postulate.

If we accept postulate IV(b), we may inquire about the meaning of the integral:

$$\int \Psi^* \hat{A} \Psi d\tau$$

Using postulate IV(b) we may replace  $\Psi(x)$  by  $\sum_n c_n \psi_n$  to give

$$\int \Psi^* \hat{A} \Psi d\tau = \int \left( \sum_n c_n \psi_n \right)^* \hat{A} \left( \sum_n c_n \psi_n \right) d\tau$$

The problem with this expression is that both summations are using the same index of summation,  $n$ . If we multiply the two sums together we will make errors, since the two values of  $n$  could be the same or they could be different. To prevent this problem let's use a different label for one of the sums:

$$\int \Psi^* \hat{A} \Psi d\tau = \int \left( \sum_n c_n \psi_n \right)^* \hat{A} \left( \sum_m c_m \psi_m \right) d\tau$$

$$= \int \left( \sum_n c_n^* \psi_n^* \right) \left( \sum_m c_m \hat{A} \psi_m \right) d\tau$$

Because  $\hat{A}$  is a linear operator

$$\int \psi^* \hat{A} \psi \, d\tau = \sum_n \sum_m c_n^* c_m \int \psi_n^* \hat{A} \psi_m \, d\tau$$

$$= \sum_n \sum_m c_n^* c_m \int \psi_n^* a_m \psi_m \, d\tau$$

[Because the  $\psi_m$  are eigenfunctions of  $\hat{A}$ , satisfying  $\hat{A}\psi_m = a_m\psi_m$ .]

$$= \sum_n \sum_m c_n^* c_m a_m \int \psi_n^* \psi_m \, d\tau$$

[Because  $a_m$  is a constant, it can be pulled out of the integral.]

Linear, Hermitian operators have many very useful properties. One that we will prove is the fact that the eigenfunctions of linear Hermitian operators are, or can be chosen to be, orthonormal.

By orthonormal we mean two things:

(1) Different eigenfunctions of the same linear Hermitian operator are orthogonal, meaning  $\int \psi_n^* \psi_m \, d\tau = 0$  if  $n \neq m$ .

and (2) the eigenfunctions are normalized, meaning  $\int \psi_m^* \psi_m \, d\tau = 1$ .

These two properties may be combined into one equation by writing

$$\int \psi_m^* \psi_n \, d\tau = \delta_{mn}, \text{ where } \delta_{mn} \text{ is}$$

the Kronecker delta, a quantity which is 0 if  $m \neq n$ , 1 if  $m = n$ .

Thus,

$$\int \psi^* \hat{A} \psi \, d\tau = \sum_n \sum_m c_n^* c_m a_m \delta_{nm}$$

$$= \sum_n c_n^* c_n a_n \text{ [Because terms with } m \neq n \text{ contribute nothing]}$$

$$\int \psi^* \hat{A} \psi d\tau = \sum_n |c_n|^2 a_n$$

According to our postulate

$|c_n|^2$  is the probability of obtaining  $a_n$  as the result of a measurement of the property A.

Thus,  $\int \psi^* \hat{A} \psi d\tau$  gives the average value that would be obtained in a series of measurements of the property A. It is called the expectation value of  $\hat{A}$ , denoted by the notation  $\langle \hat{A} \rangle$ .

### DIRAC BRACKET NOTATION:

In this course we will evaluate many integrals of the form  $\int \psi_n^* \hat{A} \psi_m d\tau$ , where the integration is carried out over all space. To simplify our notation this integral may be written in Dirac bracket notation as:

$$\int \psi_n^* \hat{A} \psi_m d\tau \equiv \langle \psi_n | \hat{A} | \psi_m \rangle$$

Here, it is implied that the function written as  $\langle \psi_n |$  must be complex conjugated before carrying out the integration which is implied. In the Dirac bracket notation,

$|\psi_m \rangle$  is called a "ket"  
and  $\langle \psi_n |$  is called a "bra"

One reason for using this notation is that the definition of a Hermitian operator becomes a bit easier to remember: A Hermitian operator can operate either on the bra or the ket to give the same result:

$$\langle \psi_n | \hat{A} | \psi_m \rangle = \langle \psi_n | \hat{A} \psi_m \rangle \quad (\text{where it is implied that } \hat{A} \text{ acts on the function } \psi_m)$$

AND

$$\langle \psi_n | \hat{A} | \psi_m \rangle = \langle \hat{A} \psi_n | \psi_m \rangle \quad (\text{where it is implied that } \hat{A} \text{ acts on } \psi_n, \text{ and the result is then complex conjugated}).$$

This nice property of Hermitian operators, namely that they can act either on the "bra" or the "ket", is what makes them useful in quantum mechanics.

## UNCERTAINTY

If a system is in a state that is an eigenfunction of an operator  $\hat{A}$  with eigenvalue  $a$ , then Postulate IV tells us that a measurement of the property  $A$  will give the value  $a$  with absolute certainty. In this case the uncertainty in  $A$  must be zero. How can we define the uncertainty in a property more generally?

In statistics, if a property is measured many times and each measurement yields a value  $x_i$  (for  $i=1, 2, 3, \dots$ ), we may define the standard deviation of our measurement as

$$\sigma = \left[ \langle x^2 \rangle - \langle x \rangle^2 \right]^{1/2} \quad \text{where } \langle x^2 \rangle \text{ and } \langle x \rangle \text{ are the averages of } x^2 \text{ and } x,$$

$$\langle x^2 \rangle = \frac{1}{N} \sum_{i=1}^N x_i^2 \quad \langle x \rangle = \frac{1}{N} \sum_{i=1}^N x_i$$

