

# Elements of Dirac Notation

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In the early days of quantum theory, P. A. M. (Paul Adrian Maurice) Dirac created a powerful and concise formalism for it which is now referred to as Dirac notation or bra-ket (bracket  $\langle \mid \rangle$ ) notation. Two major mathematical traditions emerged in quantum mechanics: Heisenberg's matrix mechanics and Schrödinger's wave mechanics. These distinctly different computational approaches to quantum theory are formally equivalent, each with its particular strengths in certain applications. Heisenberg's variation, as its name suggests, is based matrix and vector algebra, while Schrödinger's approach requires integral and differential calculus. Dirac's notation can be used in a first step in which the quantum mechanical calculation is described or set up. After this is done, one chooses either matrix or wave mechanics to complete the calculation, depending on which method is computationally the most expedient.

## Kets, Bras, and Bra-Ket Pairs

In Dirac's notation what is known is put in a ket,  $\mid \rangle$ . So, for example,  $\mid p \rangle$  expresses the fact that a particle has momentum  $p$ . It could also be more explicit:  $\mid p = 2 \rangle$ , the particle has momentum equal to 2;  $\mid x = 1.23 \rangle$ , the particle has position 1.23.  $\mid \Psi \rangle$  represents a system in the state  $\Psi$  and is therefore called the state vector. The ket can also be interpreted as the initial state in some transition or event.

The bra  $\langle \mid$  represents the final state or the language in which you wish to express the content of the ket  $\mid \rangle$ . For example,  $\langle x = .25 \mid \Psi \rangle$  is the probability amplitude that a particle in state  $\Psi$  will be found at position  $x = .25$ . In conventional notation we write this as  $\Psi(x=.25)$ , the value of the function  $\Psi$  at  $x = .25$ . The absolute square of the probability amplitude,

$|\langle x = .25 | \Psi \rangle|^2$ , is the probability density that a particle in state  $\Psi$  will be found at  $x = .25$ . Thus, we see that a bra-ket pair can represent an event, the result of an experiment. In quantum mechanics an experiment consists of two sequential observations - one that establishes the initial state (ket) and one that establishes the final state (bra).

If we write  $\langle x | \Psi \rangle$  we are expressing  $\Psi$  in coordinate space without being explicit about the actual value of  $x$ .  $\langle x = .25 | \Psi \rangle$  is a number, but the more general expression  $\langle x | \Psi \rangle$  is a mathematical function, a mathematical function of  $x$ , or we could say a mathematical algorithm for generating all possible values of  $\langle x | \Psi \rangle$ , the probability amplitude that a system in state  $|\Psi\rangle$  has position  $x$ . For the ground state of the well-known particle-in-a-box of unit dimension  $\langle x | \Psi \rangle = \Psi(x) = \sqrt{2} \sin(\pi x)$ . However, if we wish to express  $\Psi$  in momentum space we would write,  $\langle p | \Psi \rangle = \Psi(p) = \sqrt{2}\pi [\exp(-ip) + 1] / [\pi^2 - p^2]$ . How one finds this latter expression will be discussed later.

The major point here is that there is more than one language in which to express  $|\Psi\rangle$ . The most common language for chemists is coordinate space ( $x$ ,  $y$ , and  $z$ , or  $r$ ,  $\theta$ , and  $\phi$ , etc.), but we shall see that momentum space offers an equally important view of the state function. It is important to recognize that  $\langle x | \Psi \rangle$  and  $\langle p | \Psi \rangle$  are formally equivalent and contain the same physical information about the state of the system. One of the tenets of quantum mechanics is that if you know  $|\Psi\rangle$  you know everything there is to know about the system, and if, in particular, you know  $\langle x | \Psi \rangle$  you can calculate all of the properties of the system and transform  $\langle x | \Psi \rangle$ , if you wish, into any other appropriate language such as momentum space.

A bra-ket pair can also be thought of as a vector projection - the projection of the content of the ket onto the content of the bra, or the "shadow" the ket casts on the bra. For example,

$\langle \Phi | \Psi \rangle$  is the projection of the state  $\Psi$  onto the state  $\Phi$ . It is the amplitude (probability amplitude) that a system in state  $\Psi$  will be subsequently found in state  $\Phi$ . It is also what we have come to call an overlap integral.

The state vector  $|\Psi\rangle$  can be a complex function (that is have the form,  $a + ib$ , or  $\exp(-ipx)$ , for example, where  $i = \sqrt{-1}$ ). Given the relation of amplitudes to probabilities mentioned above, it is necessary that  $\langle \Psi | \Psi \rangle$ , the projection of  $\Psi$  onto itself is real. This requires that  $\langle \Psi | = |\Psi\rangle^*$ , where  $|\Psi\rangle^*$  is the complex conjugate of  $|\Psi\rangle$ . So if  $|\Psi\rangle = a + ib$  then  $\langle \Psi | = a - ib$ , which yields  $\langle \Psi | \Psi \rangle = a^2 + b^2$ , a real number.

### Ket-Bra Products - Projection Operators

Having examined kets  $| \rangle$ , bras  $\langle |$ , and bra-ket pairs  $\langle | \rangle$ , it is now appropriate to study projection operators which are ket-bra products  $| \rangle \langle |$ . Take the specific example of  $|i\rangle \langle i|$  operating on the state vector  $|\Psi\rangle$ , which is  $|i\rangle \langle i| \Psi\rangle$ . This operation reveals the contribution of  $|i\rangle$  to  $|\Psi\rangle$ , or the length of the shadow that  $|\Psi\rangle$  casts on  $|i\rangle$ .

We are all familiar with the simple two-dimensional vector space in which an arbitrary vector can be expressed as a linear combination of the unit vectors (basis vectors, basis states, etc) in the mutually orthogonal x- and y-directions. We label these basis vectors  $|i\rangle$  and  $|j\rangle$ . For the two-dimensional case the projection operator which tells how  $|i\rangle$  and  $|j\rangle$  contribute to an arbitrary vector  $|v\rangle$  is:  $|i\rangle \langle i| + |j\rangle \langle j|$ . In other words,  $|v\rangle = |i\rangle \langle i| v\rangle + |j\rangle \langle j| v\rangle$ . This

means, of course, that  $|i\rangle\langle i| + |j\rangle\langle j|$  is the identity operator:  $|i\rangle\langle i| + |j\rangle\langle j| = 1$ . This is also called the completeness condition and is true if  $|i\rangle$  and  $|j\rangle$  span the space under consideration.

For discrete basis states the completeness condition is :  $\sum_n |n\rangle\langle n| = 1$ . For continuous

basis states, such as position, the completeness condition is:  $\int |x\rangle\langle x| dx = 1$ .

If  $|\Psi\rangle$  is normalized (has unit length) then  $\langle\Psi|\Psi\rangle = 1$ . We can use Dirac's notation to express this in coordinate space as follows.

$$\langle\Psi|\Psi\rangle = \int \langle\Psi|x\rangle\langle x|\Psi\rangle dx = \int \Psi^*(x)\Psi(x)dx$$

In other words integration of  $\Psi(x)^*\Psi(x)$  over all values of x will yield 1 if  $\Psi(x)$  is normalized. Note how the continuous completeness relation has been inserted in the bra-ket pair on the left. Any vertical bar | can be replaced by the discrete or continuous form of the completeness relation. The same procedure is followed in the evaluation of the overlap integral,  $\langle\Phi|\Psi\rangle$ , referred to earlier.

$$\langle\Phi|\Psi\rangle = \int \langle\Phi|x\rangle\langle x|\Psi\rangle dx = \int \Phi^*(x)\Psi(x)dx$$

Now that a basis set has been chosen, the overlap integral can be evaluated in coordinate space by traditional mathematical methods.

### The Linear Superposition

The analysis above can be approached in a less direct but still revealing way by writing  $|\Psi\rangle$  and  $\langle\Phi|$  as linear superpositions in the eigenstates of the position operator as is shown

below.

$$|\Psi\rangle = \int |x\rangle \langle x|\Psi\rangle dx \quad \langle\Phi| = \int \langle\Phi|x'\rangle \langle x'| dx'$$

Combining these as a bra-ket pair yields,

$$\langle\Phi|\Psi\rangle = \int \int \langle\Phi|x'\rangle \langle x'|x\rangle \langle x|\Psi\rangle dx' dx = \int \langle\Phi|x\rangle \langle x|\Psi\rangle dx$$

The  $x'$  disappears because the position eigenstates are an orthogonal basis set and  $\langle x'|x\rangle = 0$  unless  $x' = x$  in which case it equals 1.

$$|\Psi\rangle = \sum_n |n\rangle \langle n|\Psi\rangle \text{ is a linear superposition in the discrete (rather than continuous)}$$

basis set  $|n\rangle$ . A specific example of this type of superposition is easy to demonstrate using matrix mechanics. For example,

$$\begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{\sqrt{2}} \left[ \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right]$$

The vector on the left represents spin-up in the x-direction, while the vectors on the right side are spin-up and spin-down in the z-direction, respectively. This can also be expressed symbolically in Dirac notation as  $|S_{xu}\rangle = \frac{1}{\sqrt{2}} [|S_{zu}\rangle + |S_{zd}\rangle]$ . It is easy to show that all three vector states are normalized, and that  $S_{zu}$  and  $S_{zd}$  form an orthonormal basis set. In other words,

$$\langle S_{zu} | S_{zu} \rangle = \langle S_{zd} | S_{zd} \rangle = 1, \text{ and } \langle S_{zu} | S_{zd} \rangle = 0.$$

It cannot be stressed too strongly that a linear superposition is not a mixture. For example, when the system is in the state  $|S_{xu}\rangle$  every measurement of the x-direction spin yields

the same result: spin-up. However, measurement of the z-direction spin yields spin-up 50% of the time and spin-down 50% of the time. The system has a well-defined value for the spin in the x-direction, but an indeterminate spin in the z-direction. It is easy to calculate the probabilities for the z-direction spin measurements:  $|\langle S_{zu} | S_{xu} \rangle|^2 = 1/2$  and  $|\langle S_{zd} | S_{xu} \rangle|^2 = 1/2$ . The reason  $|S_{xu}\rangle$  cannot be interpreted as a 50-50 mixture of  $|S_{zu}\rangle$  and  $|S_{zd}\rangle$  is because  $|S_{zu}\rangle$  and  $|S_{zd}\rangle$  are linear superpositions of  $|S_{xu}\rangle$  and  $|S_{xd}\rangle$ :  $|S_{zu}\rangle = \frac{1}{\sqrt{2}} [|S_{xu}\rangle + |S_{xd}\rangle]$ ; and  $|S_{zd}\rangle = \frac{1}{\sqrt{2}} [|S_{xu}\rangle - |S_{xd}\rangle]$ . Thus, if  $|S_{xu}\rangle$  is a mixture of  $|S_{zu}\rangle$  and  $|S_{zd}\rangle$ , it would yield an indefinite measurement of the spin in the x-direction in spite of the fact that it's an eigenfunction of the x-direction spin operator.

Just one more example of the linear superposition. Consider a trial wave function for the particle in the one-dimensional, one-bohr box such as,  $\Theta(x) = \sqrt{105} (x^2 - x^3)$ . Because the eigenfunctions for the particle-in-a-box problem form a complete basis set,  $\Phi(x)$  can be written as a linear combination or linear superposition of these eigenfunctions.

$$|\Phi\rangle = \sum_n c_n |n\rangle \quad \langle n|\Phi\rangle = \int \psi_n^* \Phi dx$$

In this notation  $\langle n|\Phi\rangle$  is the projection of  $\Phi$  onto the eigenstate n. This projection or shadow of  $\Phi$  on to n can be written as  $c_n$ . It is a measure of the contribution  $|n\rangle$  makes to the state  $|\Phi\rangle$ . It is also an overlap integral. Therefore we can write,  $|\Phi\rangle = \sum_n |n\rangle c_n$ . Using Mathcad, for example, it is easy to show that the first ten coefficients in this equation are: .935, -.351, .035, -.044, .007, -.013, .003, -.005, .001, -.003.

## Operators, Eigenvectors, Eigenvalues, and Expectation Values

In matrix mechanics operators are matrices and states are represented by vectors. The matrices operate on the vectors to obtain useful physical information about the state of the system. According to quantum theory there is an operator for every physical observable and a system is either in a state with a well-defined value for that observable or it is not.

The operators associated with spin in the x- and z-direction are shown below in units of  $\hbar/4\pi$ .

$$\hat{S}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{S}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

When  $\hat{S}_x$  operates on  $|S_{xu}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$  the result is  $S_{xu}$ :  $\hat{S}_x |S_{xu}\rangle = |S_{xu}\rangle$ .  $S_{xu}$  is an

eigenfunction or eigenvector of  $\hat{S}_x$  with eigenvalue 1 (in units of  $\hbar/4\pi$ ). However,  $S_{xu}$  is not an

eigenfunction of  $\hat{S}_z$  because  $\hat{S}_z |S_{xu}\rangle = |S_{xd}\rangle$  where  $|S_{xd}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$ . This means, as

mentioned in the previous section, that  $S_{xu}$  does not have a definite value for spin in the z-direction. Under these circumstances we can't predict with certainty the outcome of a z-direction spin measurement, but we can calculate the average value for a large number of measurements.

This is called the expectation value and in Dirac notation it is represented as

follows:  $\langle S_{xu} | \hat{S}_z | S_{xu} \rangle = 0$ . In matrix mechanics it is calculated as follows.

$$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = 0$$

This result is consistent with the previous discussion which showed that  $|S_{xu}\rangle$  is a 50-50 linear superposition of  $|S_{zu}\rangle$  and  $|S_{zd}\rangle$  with eigenvalues of +1 and -1, respectively. In other words, half the time the result of the measurement is +1 and the other half -1, yielding an average value of zero.

Now we will look at the calculation for the expectation value for a system in the state  $|\Psi\rangle$ , which is set up as follows:  $\langle\Psi|\hat{x}|\Psi\rangle$ . To make this calculation computationally friendly we expand  $|\Psi\rangle$  in the eigenstates of the position operator.

$$\langle\Psi|\hat{x}|\Psi\rangle = \int \langle\Psi|\hat{x}|x\rangle\langle x|\Psi\rangle dx = \int \langle\Psi|x\rangle x \langle x|\Psi\rangle dx = \int \Psi(x)^* x \Psi(x) dx$$

Note the simplification that occurs because  $\hat{x}|x\rangle = x|x\rangle = |x\rangle x$

### The Variation Method

We have had a preliminary look at the variation method, an approximate method used when an exact solution to Schrödinger's equation is not available. Using  $\Phi(x) = \sqrt{30}x(1-x)$  as a trial wave function for the particle-in-the-box problem, we evaluate the expectation value for the energy as  $\langle E \rangle = \langle \Phi | \hat{H} | \Phi \rangle$ . However, employing Dirac's formalism we can expand  $\Phi$ , as noted above, in terms of the eigenfunctions of  $H$  as follows.

$$\langle E \rangle = \langle \Phi | \hat{H} | \Phi \rangle = \sum_n \langle \Phi | \hat{H} | n \rangle \langle n | \Phi \rangle$$

But,  $\hat{H}|n\rangle = E_n|n\rangle$  because the states  $|n\rangle = \sqrt{2} \sin(n\pi x)$  are eigenfunctions of the energy operator,  $\hat{H}$ . Thus, the energy expression becomes,

$$\langle E \rangle = \sum_n \langle \Phi | n \rangle E_n \langle n | \Phi \rangle = \sum_n |c_n|^2 E_n$$

where  $E_n = \frac{n^2 \pi^2}{2}$ . Because  $\Phi$  is not an eigenfunction of  $\hat{H}$ , the energy operator, this system

does not have a well-defined energy and all we can do is calculate the average value for many experimental measurements of the energy. Each individual energy measurement will yield one of the eigenvalues of the energy operator,  $E_n$ , and the  $|c_n|^2$  tells us the probability of this result being achieved. Using Mathcad it is easy to show that  $c_1^2 = .9987$ ,  $c_3^2 = .0014$ ,  $c_5^2 = .00006$ , and  $c_7^2 = .00001$ . All other coefficients are zero or vanishingly small. These results say that if we make an energy measurement on a system in the state represented by  $\Phi$  there is a 99.87% chance we will get 4.935, a 0.14% chance we will get 19.739, and so on. We might say then that the state  $\Phi$  is a linear combination of the first four odd eigenfunctions, with the first eigenfunction making by far the biggest contribution.

The variational theorem says that no matter how hard you try in constructing trial wave functions you can't do better than the 'true' ground state value for the energy, and this equation captures that important principle. The only way  $\Phi$  can give the correct result for the ground state of the particle in the box, for example, is if  $c_1 = 1$ , or if  $\Phi$  is the eigenfunction itself. If this is not true, then  $c_1 < 1$  and the other values of  $c$  are non-zero and the energy has to be greater than  $E_1$ .

Taking another look at the last two equations reveals that a measurement operator can always be written as a projection operator involving its eigenstates,  $\hat{H} = \sum_n |n\rangle E_n \langle n|$ .

### Momentum Operator in Coordinate Space

Wave-particle duality is at the heart of quantum mechanics. A particle with wavelength  $\lambda$  has wave function (un-normalized)  $\langle x | \lambda \rangle = \exp\left(i2\pi \frac{x}{\lambda}\right)$ . However, according to deBroglie's wave equation

the particle's momentum is  $p = h/\lambda$ . Therefore the momentum wave function of the particle in coordinate space is  $\langle x | p \rangle = \exp\left(\frac{ipx}{\hbar}\right)$ .

In momentum space the following eigenvalue equation holds:  $\hat{p} | p \rangle = p | p \rangle$ . Operating on the

momentum eigenfunction with the momentum operator in momentum space returns the momentum eigenvalue times the original momentum eigenfunction. In other words, in its own space the momentum operator is a multiplicative operator (the same is true of the position operator in coordinate space). To obtain the momentum operator in coordinate space this expression can be projected onto coordinate space by operating on the left by  $\langle x|$ .

$$\langle x|\hat{p}|p\rangle = p\langle x|p\rangle = p \exp\left(\frac{ipx}{\hbar}\right) = \frac{\hbar}{i} \frac{d}{dx} \exp\left(\frac{ipx}{\hbar}\right) = \frac{\hbar}{i} \frac{d}{dx} \langle x|p\rangle$$

Comparing the first and last terms reveals that

$$\langle x|\hat{p} = \frac{\hbar}{i} \frac{d}{dx} \langle x|$$

and that  $\frac{\hbar}{i} \frac{d}{dx}$  is the momentum operator in coordinate space.  $\langle p|x\rangle = \exp\left(\frac{-ipx}{\hbar}\right)$  is the

position wave function in momentum space. Using the method outlined above it is easy to show

that the position operator in momentum space is  $-\frac{\hbar}{i} \frac{d}{dp}$ .

### Fourier Transform

Quantum chemists work mainly in position (x,y,z) space because they are interested in electron densities, how the electrons are distributed in space in atoms and molecules. However, quantum mechanics has an equivalent formulation in momentum space. It answers the question of what does the distribution of electron velocities look like? The two formulations are equivalent, that is, they contain the same information, and are connected formally through a Fourier transform. The Dirac notation shows this connection very clearly.

$$\langle p|\Psi\rangle = \int \langle p|x\rangle \langle x|\Psi\rangle dx$$

Starting from the left we have the amplitude that a system in state  $\Psi$  has position x. Then, if it has position x, the amplitude that it has momentum p. We then sum over all values of x to find all the

ways a system in the state  $\Psi$  can have momentum  $p$ . As a particular example we can choose the particle-in-a-box problem with eigenfunctions  $\langle x | \Psi \rangle$  noted above. It is easy to show that the momentum eigenstates in position space in atomic units (see previous section) are

$\langle x | p \rangle = \exp(ipx)$ . This, of course, means that the complex conjugate is

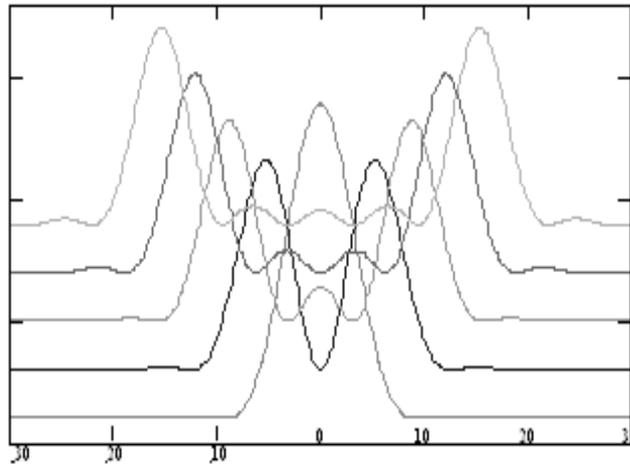
$\langle p | x \rangle = \exp(-ipx)$ . Therefore, the Fourier transform of  $\Psi(x)$  into momentum space is

$$\langle p | \Psi \rangle = \Psi(p) = \frac{1}{\sqrt{2\pi}} \int_0^1 \exp(-ipx) \sqrt{2} \sin(n\pi x) dx$$

This integral can be evaluated analytically and yields the following momentum space wave functions for the particle-in-a-box.

$$\langle p | \Psi \rangle = \Psi(p) = n\sqrt{\pi} \left[ \frac{1 - \cos(n\pi) \exp(-ip)}{n^2 \pi^2 - p^2} \right]$$

A graphical display of the momentum distribution function,  $\Psi^*(p)\Psi(p)$ , for several states is shown below.



## Summary and References

J. L. Martin (see references below) has identified four virtues of Dirac notation.

1. It is concise. There are a small number of basic elements to Dirac's notation: bras, kets, bra-ket pairs, ket-bra products, and the completeness relation (continuous and discrete). With these few building blocks you can construct all of quantum theory.
2. It is flexible. You can use it to say the same thing in several ways; translate with ease from one language to another. Perhaps the insight that the Dirac notation offers to the Fourier transform is the best example of this virtue.
3. It is general. It is a syntax for describing what you want to do without committing yourself to a particular computational approach. In other words, you use it to set up a problem and then choose the most expeditious way to execute the calculation.
4. While it is not exactly the industry standard, it should be for the reasons listed in 1-3 above. It is widely used, so if you want to read the literature in quantum chemistry and physics, you need to learn Dirac notation. In addition most of the best quantum textbooks in chemistry and physics use it.

I would like to add a 5<sup>th</sup> virtue.

5. Once you get the "hang of it" you will find that it is simple to use and very enlightening. It facilitates the understanding of all the fundamental quantum concepts.

The following texts have been used in preparing this tutorial:

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