

# Physics 123 Lecture Notes

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# Chapter 0

## Dirac Notation

This review covers the use of Dirac notation, which is used in many of the chapters that follow. Much of this material may serve only as a refresher of things students have already seen in other courses.

### 0.1 States

When physics students are introduced to quantum mechanics, most are first presented with the spatial wavefunction and told that this is the way we describe the states of quantum systems. By *spatial wavefunction*, what I mean is the function that is almost universally called  $\psi(\mathbf{r})$ , where  $\mathbf{r}$  stands for one or more spatial degrees of freedom that are often associated with the “position” of the system. Familiar examples include the location of a particle in a potential well, or the position of an electron in an atom.

Students are told that the wavefunction is normalized according to

$$\int d^3\mathbf{r} \psi^*(\mathbf{r})\psi(\mathbf{r}) = \int d^3\mathbf{r} |\psi(\mathbf{r})|^2 = 1 \quad (1)$$

and that

$$d\mathcal{P}(\mathbf{r}) = |\psi(\mathbf{r})|^2 d^3\mathbf{r} \quad (2)$$

is the differential probability of finding the system’s position in a volume  $d^3\mathbf{r}$  centered at position  $\mathbf{r}$ . (Here, I am using  $d^3\mathbf{r}$  to denote a differential volume element, such as  $d^3\mathbf{r} = dx dy dz$  in Cartesian coordinates or  $d^3\mathbf{r} = d\phi d\theta dr \sin(\theta)r^2$  in spherical coordinates.)

However, upon advancing further in the subject, physics students are eventually confronted with the fact that  $\psi(\mathbf{r})$  is not really the *state* of the system so much as it is a particular *representation* of the state –  $\psi(\mathbf{r})$  is a representation of the state as a probability amplitude in position space. To illustrate the distinction we’re driving at, consider the familiar position-space wavefunction for the stationary states of the 1D Infinite Square Well (or “particle in a box”) that spans from  $-L/2 \leq x \leq L/2$ ,

$$\psi_n^{(\text{ISW})}(x) = \sqrt{\frac{2}{L}} \sin\left(n\pi \left(\frac{x}{L} + \frac{1}{2}\right)\right). \quad (3)$$

Just as any sufficiently well-behaved function  $f(x)$  can be Fourier transformed into a new function  $\tilde{f}(k)$ , we can also consider writing the wavefunctions of the stationary states of the infinite square well as a functions of translational momentum,

$$\tilde{\psi}_n^{(\text{ISW})}(p_x) = \frac{i}{2} \sqrt{\frac{L}{\pi\hbar}} \left[ (-i)^n \text{sinc}\left(\frac{L}{2\hbar}p_x + n\frac{\pi}{2}\right) - (i)^n \text{sinc}\left(\frac{L}{2\hbar}p_x - n\frac{\pi}{2}\right) \right] \quad (4)$$

where  $\text{sinc}(x) \equiv \sin(x)/x$ . Both versions are shown for the first few levels in Figure 1.

These two different functions, (3) and (4), are *both* correct ways to write the wavefunction of a particle in an infinite square well. Both of them are normalized, and they both represent probability density; for the general, 3D case with momentum-space wavefunction  $\tilde{\psi}(\mathbf{p})$ , the quantity  $|\tilde{\psi}(\mathbf{p})|^2 d^3\mathbf{p}$  is the differential probability that the momentum of the system is found in a volume  $d^3\mathbf{p}$  centered at momentum  $\mathbf{p}$ . Any prediction, expectation value, transition probability, *etc.* that one can calculate from  $\psi(\mathbf{r})$ , one could likewise calculate from  $\tilde{\psi}(\mathbf{p})$ , and the choice is largely one of calculational convenience.

Since we have two, *different* wavefunctions that somehow both fully-describe the same state, it is natural to wonder if there is a more abstract object that we might call the *quantum state* from which both of these wavefunctions can be derived as properties.

The answer is yes. Quantum states, unlike wavefunctions, do not live in position space, or momentum space – they are vectors in a type of abstract linear vector space called a *Hilbert space*. Now, even though we’re not really going to get into what this Hilbert space is, I want to be clear that when I

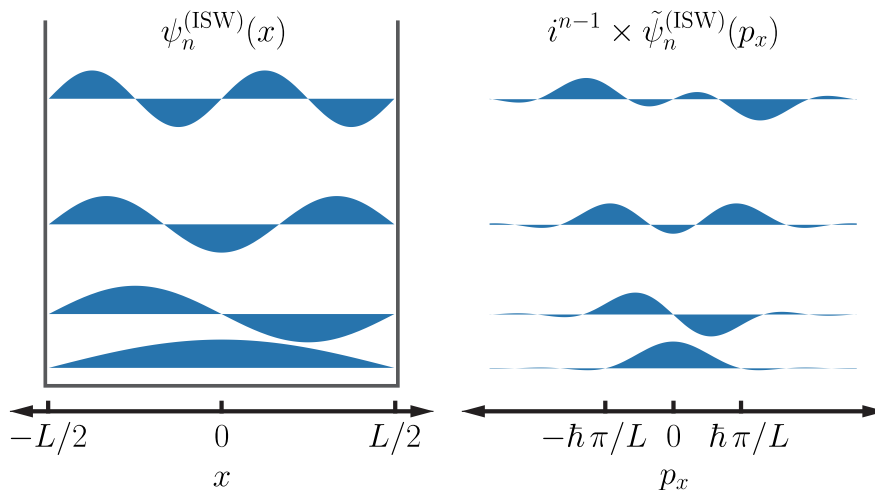


Figure 1: Schematic showing the first four energy-eigenstate wavefunctions for a particle in a 1D infinite square well. The position-space wavefunctions (left) and momentum-space wavefunctions (right) are both shown, offset vertically by their energy eigenvalues.

say *vectors*, here, I do not mean  $\mathbf{r}$  or  $\mathbf{p}$ . What we’re talking about are unit vectors in a multi-dimensional space where each axis is a unique element of a complete, orthonormal basis that could be used to describe the quantum state of the system.

However, all of that is beyond the scope of this course, and the point is that we want a name for this “quantum state” that is the parent of these wavefunctions and we need to figure out how to work with it. And for that, we are going to use Dirac notation.

## 0.2 Dirac notation

I will assume that you have at least seen Dirac notation before and remind you that the idea is that the states are written as labels that live in these funny brackets called “bras” (such as  $\langle A|$  or  $\langle \psi|$ ) and “kets” (such as  $|A\rangle$  or  $|\psi\rangle$ ). Though it doesn’t have to be this way, it may be helpful for you to think about kets as being represented by column vectors and bras as being

represented by row vectors with dimensionless, complex entries,

$$|B\rangle \doteq \begin{pmatrix} B_1 \\ B_2 \\ \vdots \\ B_N \end{pmatrix} \quad (5)$$

$$\langle B| = \left(|B\rangle\right)^\dagger \doteq (B_1^*, B_2^*, \dots, B_N^*), \quad (6)$$

where  $\doteq$  means “can be represented by” and I have introduced the superscript dagger ( $^\dagger$ ) to denote the Hermitian conjugate (which becomes the conjugate transpose in the matrix representation), which converts between the two. To find the Hermitian conjugate of a matrix or column/row vector, take its transpose and then replace each element with its complex conjugate.

The details of what the entries in these vectors are (and how many of them there are) will depend upon the set of basis vectors that are chosen to make such a representation, but we will ignore all of that for now and it’s okay to think of the above as a good mental picture of the difference between bras and kets.

### 0.2.1 Properties of bras and kets

There are some rules to keep in mind when working with bras and kets, most of which are easier to see if we imagine these are unit vectors represented as column or row vectors as shown above. Kets can be added and subtracted from one another (as can bras), to make new kets (or bras),

$$|A\rangle + |B\rangle = |C\rangle.$$

When considering their representation as a column vector, this simply means we add the entries,

$$\begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} + \begin{pmatrix} B_1 \\ B_2 \\ \vdots \\ B_N \end{pmatrix} = \begin{pmatrix} A_1 + B_1 \\ A_2 + B_2 \\ \vdots \\ A_N + B_N \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_N \end{pmatrix}.$$

What about adding a bra to a ket? Well, visualizing these as column and row vectors, it becomes clear that there is no well-defined way to do this:

$$\begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} + (B_1^*, B_2^*, \dots, B_N^*) = ?$$

So if you are at some point working through a problem and you find yourself faced with an expression that looks like  $a\langle A| + b|B\rangle$ , it means something went wrong in your calculation and you need to reexamine your previous steps. (This is a little bit like dimensional analysis in classical mechanics, where if you realize you're trying to add a position to a mass, something went wrong!)

Kets can also be multiplied by dimensionless complex numbers, and those pure numbers commute with the kets:

$$a|A\rangle = |A\rangle a. \quad (7)$$

(The special case in which  $a = 0$  occurs frequently, and you can think of the result as being the *null ket*, which is almost always omitted in the same way that we often omit terms that are 0 from sums instead of explicitly writing “+ 0.”) Note that the bra that is dual to  $a|A\rangle$  is  $a^*\langle A|$ , not  $a\langle A|$ .

### 0.2.2 Inner product

Next, we define an operation called the *inner product* that can be taken between a bra and a ket, the result of which is a dimensionless complex number. The notation for the inner product of  $\langle A|$  and  $|B\rangle$  is

$$\langle A|B\rangle.$$

This is related to the inner product of  $\langle B|$  and  $|A\rangle$  via

$$\langle B|A\rangle = (\langle A|B\rangle)^* \quad (8)$$

where the  $*$  denotes the simple complex conjugate, as the thing in parentheses is just a complex number.

Much like the case with real-space unit vectors  $\hat{\mathbf{q}}$  where we require that the inner product with itself is  $\hat{\mathbf{q}} \cdot \hat{\mathbf{q}} = 1$ , we likewise require that normalized kets (and normalized bras) obey

$$\langle A|A\rangle = 1. \quad (9)$$

In the column vector representation introduced above, this amounts to

$$\begin{aligned} (A_1^*, A_2^*, \dots, A_N^*) \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} &= A_1^* A_1 + A_2^* A_2 + \dots + A_N^* A_N \\ &= |A_1|^2 + |A_2|^2 + \dots + |A_N|^2 \\ &= 1. \end{aligned}$$

This is the Dirac notation version of the normalization condition, Eq. (1).

Further, much like the way we find the projection of real-space vectors using the dot product, the inner product can be used to find the component of one ket ( $|A\rangle$ ) along another ( $|B\rangle$ ) via

$$\langle B|A\rangle. \quad (10)$$

This quantity is the probability amplitude that if we measure a system that starts in the state  $|A\rangle$  in such a way as to determine if it is in  $|B\rangle$ , we find that it is. If we want the *probability* that a measurement of whether a system in state  $|A\rangle$  is found in  $|B\rangle$ , we take the abs-squared of this projection.

### 0.2.3 Outer product

Much like the inner product, which yielded a scalar, it is possible to construct an *outer product* of a ket with a bra,

$$|A\rangle\langle B|,$$

which is an operator. In matrix representation, the outer product is a matrix:

$$\begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} (B_1^*, B_2^*, \dots, B_N^*) = \begin{pmatrix} A_1 B_1^* & A_1 B_2^* & \dots & A_1 B_N^* \\ A_2 B_1^* & A_2 B_2^* & \dots & A_2 B_N^* \\ \vdots & \vdots & \ddots & \vdots \\ A_N B_1^* & A_N B_2^* & \dots & A_N B_N^* \end{pmatrix}. \quad (11)$$

The outer product of a vector with itself is a *projector* onto that vector,

$$\hat{P}_A = |A\rangle\langle A|, \quad (12)$$



as this will pick out only the projection of any vector it operates upon along  $|A\rangle$  (or  $\langle A|$  if it operates from the right on a bra).

The outer product is particularly useful for expressing operators in the basis of the states they operate on. For example, if we happen to know that the energy eigenvalues of some two-state system are  $E_a$  and  $E_b$  for the two eigenstates  $|\psi_a\rangle$  and  $|\psi_b\rangle$ , we can replace the detailed Hamiltonian (which might be some complicated function with things like  $\mathbf{p}^2$  and  $V(\mathbf{r})$  in it) with a *phenomenological Hamiltonian*,

$$H = E_a |\psi_a\rangle\langle\psi_a| + E_b |\psi_b\rangle\langle\psi_b|.$$

Here, the number of terms is equal to the number of basis states required to describe the system. If we have a complete list of energy eigenstates and their eigenvalues, we can write

$$H = \sum_i E_i |\psi_i\rangle\langle\psi_i|. \quad (13)$$

This invites the matrix representation of the phenomenological Hamiltonian in diagonal form

$$H \doteq \begin{pmatrix} E_1 & 0 & \cdots & 0 \\ 0 & E_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & E_N \end{pmatrix} \quad (14)$$

Likewise, the identity operator (or, in matrix representation, the identity matrix) can be written as a sum over discrete orthonormal basis states,

$$\mathbb{1} = \sum_i |\psi_i\rangle\langle\psi_i| \quad (15)$$

or as an integral over continuous, orthonormal basis states,

$$\mathbb{1} = \int d^3\mathbf{r} |\mathbf{r}\rangle\langle\mathbf{r}|. \quad (16)$$

## 0.3 Wavefunctions

So, what is the connection between these abstract bras and kets and wavefunctions like  $\psi(x)$ ? It turns out that the quantum state of the system, which we might denote as  $|\psi\rangle$ , can be used to determine the system's wavefunctions. To find out how, we will first need to introduce *position eigenstates*.

### 0.3.1 Position eigenstates

An eigenket of an operator  $\hat{M}$  is a ket that obeys the relation

$$\hat{M}|A\rangle = m|A\rangle$$

where  $m$  is a (potentially dimensional) constant. When such a ket is the state of a quantum system, we call it an eigenstate of  $\hat{M}$ , and it is typical that the label inside the ket will include the eigenvalue  $m$  somehow as a reminder (e.g.  $|A, m\rangle$ ).

A *position eigenstate*  $|\mathbf{r}_0\rangle$  is an eigenstate of the position operator,  $\mathbf{r}$  (We omit the hat here to avoid introducing confusion with unit vectors), with eigenvalue  $\mathbf{r}_0$ :

$$\mathbf{r}|\mathbf{r}_0\rangle = \mathbf{r}_0|\mathbf{r}_0\rangle. \quad (17)$$

It is also an eigenstate of the *components* of  $\mathbf{r}$ , such as

$$\hat{y}|\mathbf{r}_0\rangle = y_0|\mathbf{r}_0\rangle.$$

The position eigenstate  $|\mathbf{r}_0\rangle$  is the state of a quantum system whose position is known to be precisely at  $\mathbf{r}_0$ . (As a result, its momentum spread is infinite.) Though this sounds somewhat nonphysical, we're not ever going to claim that any real quantum system is in a position eigenstate – what we're interested in is the representation of a quantum state as a *superposition* of position eigenstates, so we're going to allow  $\mathbf{r}_0$  to be a variable (and will therefore often just call it  $\mathbf{r}$ ).

So if we want to know the differential probability that a quantum system in some state  $|\psi\rangle$  is going to be found inside a differential volume  $d^3\mathbf{r}$  centered at position  $\mathbf{r}$  if its position is measured, we can use equation (10) to calculate the overlap between the state of the system and the position eigenstate at  $\mathbf{r}$ :

$$d\mathcal{P}(\mathbf{r}) = |\langle\mathbf{r}|\psi\rangle|^2 d^3\mathbf{r}.$$

If we compare this to the way we calculated it in Eq. (2) given a wavefunction  $\psi(\mathbf{r})$ ,

$$d\mathcal{P}(\mathbf{r}) = |\psi(\mathbf{r})|^2 d^3\mathbf{r},$$

we see that

$$|\psi(\mathbf{r})|^2 = |\langle\mathbf{r}|\psi\rangle|^2.$$

The position-space wavefunction is the projection of the *state vector* (here  $|\psi\rangle$ ) on the position eigenstate  $|\mathbf{r}\rangle$  where we allow  $\mathbf{r}$  to be a variable:

$$\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle. \quad (18)$$

Remember, the state vector  $|\psi\rangle$  is *not* a function of  $\mathbf{r}$ ; only  $\psi(\mathbf{r})$  is a function of  $\mathbf{r}$ , so it's best to avoid notation like  $|\psi(\mathbf{r})\rangle$  (though you will see this from time to time, particularly when  $\mathbf{r}$  has a subscript that the author wants to associate with the ket).

As a consistency check on all of this, we can try to recover the integral form of, for instance, the normalization condition (1) by starting with (9). We have

$$\begin{aligned} \langle \psi | \psi \rangle &= \langle \psi | \mathbb{1} | \psi \rangle \\ &= \langle \psi | \int d^3\mathbf{r} |\mathbf{r}\rangle \langle \mathbf{r}| | \psi \rangle \\ &= \int d^3\mathbf{r} \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | \psi \rangle \\ &= \int d^3\mathbf{r} \psi^*(\mathbf{r}) \psi(\mathbf{r}), \end{aligned}$$

where I have used (16).

Though it is not common to need it, Eq. (18) can be inverted to express the state vector in terms of a wavefunction,

$$\begin{aligned} |\psi\rangle &= \int d^3\mathbf{r} \psi(\mathbf{r}) |\mathbf{r}\rangle \\ \langle \psi | &= \int d^3\mathbf{r} \psi^*(\mathbf{r}) \langle \mathbf{r} |. \end{aligned} \quad (19)$$

Written this way, it is perhaps more clear what a wavefunction *is* – it's a collection of coefficients that give the probability amplitudes for the state to be in each of a collection of basis states (in this case, of an orthonormal continuous position basis).

Last, what's the spatial wavefunction of a position eigenstate (such as  $|\mathbf{r}_0\rangle$ )? Well, if we call this wavefunction  $\langle \mathbf{r} | \mathbf{r}_0 \rangle = \psi_{\mathbf{r}_0}(\mathbf{r})$ , we can use the definition of the wavefunction of some other state  $|\psi\rangle$  to see that

$$\langle \mathbf{r}_0 | \psi \rangle = \int d^3\mathbf{r} \psi_{\mathbf{r}_0}^*(\mathbf{r}) \psi(\mathbf{r}).$$

Since we require that this integral yield  $\psi(\mathbf{r}_0)$ , the only thing that  $\psi_{\mathbf{r}_0}^*(\mathbf{r})$  can be is

$$\psi_{\mathbf{r}_0}^*(\mathbf{r}) = \langle \mathbf{r}_0 | \mathbf{r} \rangle = \delta(\mathbf{r} - \mathbf{r}_0).$$

So the spatial wavefunction of a position eigenstate  $|\mathbf{r}_0\rangle$  is

$$\langle \mathbf{r} | \mathbf{r}_0 \rangle = \delta(\mathbf{r} - \mathbf{r}_0). \quad (20)$$

This, with some caveats<sup>1</sup>, might make some sense to you. Finding the overlap between position eigenkets is like asking: if the particle is infinitely localized at position  $\mathbf{r}$ , what is the probability amplitude for it to be found at position  $\mathbf{r}_0$ ? That should be zero everywhere except for when  $\mathbf{r}_0 = \mathbf{r}$ , at which point it needs to blow up enough so that the total probability of the particle being found anywhere in all of space integrates to 1.

### 0.3.2 Other types of wavefunctions

In much the same manner as we did for finding the position eigenstate of the state  $|\psi\rangle$  by taking the inner product (also called the “overlap integral”) with a position eigenstate, we could construct a momentum eigenstate,

$$\mathbf{p} |\mathbf{p}_0\rangle = \mathbf{p}_0 |\mathbf{p}_0\rangle$$

and use this to obtain the momentum-space wavefunction of the same state:

$$\tilde{\psi}(\mathbf{p}) = \langle \mathbf{p} | \psi \rangle. \quad (21)$$

Comparing Eq. (4) to (3), we see that the position and momentum wavefunctions are *related* to one another, but are generally not the same mathematical function with different variables plugged in.

### 0.3.3 Superposition states

We have already been more-or-less dancing around the idea that the quantum state of a system may be written as a *superposition* of allowed state vectors.

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<sup>1</sup>Here, the reader is cautioned that this expression should only really be used inside an integral such that one of the two  $\mathbf{r}$ s changes along with the integration variable. Don’t try to use this formula to calculate  $\langle \mathbf{r} | \mathbf{r} \rangle$ , as the normalization of these position eigenstates is not the normal thing.

If we take an orthonormal, complete basis set of allowed states  $\{|\phi_i\rangle\}$ , such a superposition might look like

$$\begin{aligned} |\psi\rangle &= A_1|\phi_1\rangle + A_2|\phi_2\rangle + \cdots + A_N|\phi_N\rangle \\ &= \sum_i A_i|\phi_i\rangle \end{aligned} \quad (22)$$

for complex, dimensionless numbers  $\{A_i\}$ . Normalization of this amounts to  $\sum_i |A_i|^2 = 1$ .

If we are given  $|\psi\rangle$  and we wish to find one of these expansion coefficients, we can simply operate on the above from the left with the basis bra corresponding to that coefficient. For example, to find  $A_2$ , we operate on the left with  $\langle\phi_2|$ :

$$\begin{aligned} \langle\phi_2||\psi\rangle &= \langle\phi_2|A_1|\phi_1\rangle + \langle\phi_2|A_2|\phi_2\rangle + \cdots + \langle\phi_2|A_N|\phi_N\rangle \\ \langle\phi_2|\psi\rangle &= A_1\langle\phi_2|\phi_1\rangle + A_2\langle\phi_2|\phi_2\rangle + \cdots + A_N\langle\phi_2|\phi_N\rangle \\ &= A_1 \times 0 + A_2 \times 1 + \cdots + A_N \times 0 \\ &= A_2 \end{aligned}$$

and we find that

$$A_i = \langle\phi_i|\psi\rangle. \quad (23)$$

Here, we see that the column-vector representation of the state  $|\psi\rangle$  can be defined in terms of the basis bras  $\{|\phi_i\rangle\}$  by assigning each row to a unique index  $i$ :

$$|\phi_1\rangle \doteq \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \quad |\phi_2\rangle \doteq \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix} \quad \cdots \quad |\phi_N\rangle \doteq \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix} \quad (24)$$

$$|\psi\rangle \doteq \begin{pmatrix} A_1 \\ A_2 \\ \vdots \\ A_N \end{pmatrix} = \begin{pmatrix} \langle\phi_1|\psi\rangle \\ \langle\phi_2|\psi\rangle \\ \vdots \\ \langle\phi_N|\psi\rangle \end{pmatrix}. \quad (25)$$

### 0.3.4 Product states

When a system has multiple degrees of freedom, it may be convenient to write its state vector in terms of separate state vectors that could describe the states of each degree of freedom independently. We do this by “multiplying” those state vectors together to make a product, but the type of product we’re referring to is something called a *tensor product*. This may sound very fancy and advanced, but all it really means is that we will keep track of labels that tell us which degree of freedom we’re talking about.

For example, when solving the time-independent Schrödinger equation to find the energy eigenstates of the hydrogen atom, the technique of *separation of variables* is typically invoked; the spatial wavefunction ( $\psi(\mathbf{r})$ ) is split up into the product of a radial wavefunction (often called  $R_{nL}(r)$ ) and the angular wavefunction (typically given by spherical harmonics  $Y_{LM}(\theta, \phi)$ ),

$$\psi_{nLM}(\mathbf{r}) = R_{nL}(r)Y_{LM}(\theta, \phi). \quad (26)$$

For wavefunctions, these products are literally just products – two mathematical functions multiplied together in the regular way – and it would be a little surprising if the term “tensor product” were even used at that stage of instruction.

For *state vectors* like bras and kets, we will write product states of multiple degrees of freedom either as cascaded vectors (such as  $|\psi\rangle|\phi\rangle$  or  $\langle\psi|\langle\phi|$ ) or as multiple labels within a single vector (as in  $|\psi, \phi\rangle$ , sometimes with a comma or semicolon, sometimes without)<sup>2</sup>. The important thing is that the two vectors describe *different* degrees of freedom of the system whose state is being described, such as the dependence on different variables, or maybe two different objects like spin  $A$  and spin  $B$ . For the hydrogen atom example above, we’d write the more-general statement about the states themselves (as opposed to their representation in terms of spatial wavefunctions) as

$$|\psi_{nLM}\rangle = |R_{nL}\rangle|L M\rangle = |n L M\rangle.$$

To connect this back to wavefunctions, we can pull out the dependence on only one variable by operating with variable eigenstates. For example, if

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<sup>2</sup>You will also probably at some point encounter an explicit tensor product symbol,  $\otimes$ , that gets used to denote the same thing (such as  $|\psi\rangle \otimes |\phi\rangle$ ), but we will try to avoid this flourish unless it is necessary for clarity.

we want the spatial wavefunction for only the angular variables  $\boldsymbol{\omega} \equiv (\theta, \phi)$ , we could write

$$\langle \boldsymbol{\omega} | \psi_{nLM} \rangle = \langle \boldsymbol{\omega} | R_{nL} \rangle |L M\rangle = |R_{nL}\rangle \langle \boldsymbol{\omega} | L M\rangle = Y_{LM}(\boldsymbol{\omega}) |R_{nL}\rangle,$$

whereas for the radial wavefunction, we could write

$$\langle r | \psi_{nLM} \rangle = \langle r | R_{nL} \rangle |L M\rangle = R_{nL}(r) |L M\rangle. \quad (27)$$

To get both, we just use all of the components of  $\mathbf{r}$ :

$$\langle \mathbf{r} | \psi_{nLM} \rangle = \langle \mathbf{r} | R_{nL} \rangle |L M\rangle = \langle \mathbf{r} | \langle \boldsymbol{\omega} | R_{nL} \rangle |L M\rangle = R_{nL}(r) Y_{LM}(\boldsymbol{\omega}). \quad (28)$$

Note that if the state is a *superposition of product basis states*, this gets a little more complex, as in

$$\begin{aligned} \langle \mathbf{r} | \frac{1}{\sqrt{2}} (|\psi_{nLM}\rangle + |\psi_{n'L'M'}\rangle) &= \frac{1}{\sqrt{2}} \langle \mathbf{r} | R_{nL} \rangle |L M\rangle + \frac{1}{\sqrt{2}} \langle \mathbf{r} | R_{n'L'} \rangle |L' M'\rangle \\ &= \frac{1}{\sqrt{2}} R_{nL}(r) |L M\rangle + \frac{1}{\sqrt{2}} R_{n'L'}(r) |L' M'\rangle. \end{aligned} \quad (29)$$

Here, assuming that  $(L, M) \neq (L', M')$ , there *is* no single “radial wavefunction” associated with the state above due to the presence of something called *quantum entanglement*. The radial state depends on the angular state, so there is no way to assign a meaningful wavefunction to it by itself. To put it another way, the quantum state of the distance between the nucleus and the electron cannot be written as a wavefunction – it is some other, more-exotic type of quantum state called a *mixed state* that is not within our scope for this class.

## 0.4 Matrix elements

Most physics students are taught that to take an expectation value of an operator ( $\hat{M}$ ), they should use the wavefunction ( $\psi_a(\mathbf{r})$ ) to compute the following spatial integral,

$$\langle \hat{M} \rangle = \int d^3\mathbf{r} \psi_a^*(\mathbf{r}) \hat{M} \psi_a(\mathbf{r}).$$

Based on the discussion above, it is also clear that this integral could be done using momentum-space wavefunctions (though the form of the operator will often also need to be changed).

This is a special case of a *matrix element* of  $\hat{M}$ . A matrix element of an operator is a (possibly dimensionful) complex number that is defined relative to a particular bra and a particular ket. Working with wavefunctions in the spatial domain, the  $a, b$  matrix element of operator  $\hat{M}$  would be given by

$$M_{ab} = \int d^3\mathbf{r} \psi_a^*(\mathbf{r}) \hat{M} \psi_b(\mathbf{r}). \quad (30)$$

The idea is that these numbers could be written as the elements of a matrix representation of  $\hat{M}$  in the basis that includes these states as basis vectors:

$$\hat{M} \doteq \begin{pmatrix} M_{aa} & M_{ab} & \cdots \\ M_{ba} & M_{bb} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (31)$$

Clearly,  $M_{aa}$  (which is known as a *diagonal matrix element*) is just the expectation value of  $\hat{M}$  in state  $a$ .

Using our correspondences from the discussion above, we can likewise write the matrix elements in Dirac notation as

$$M_{ab} = \langle \psi_a | \hat{M} | \psi_b \rangle, \quad (32)$$

which allows us to represent  $\hat{M}$  in matrix form via

$$\hat{M} \doteq \begin{pmatrix} \langle \psi_a | \hat{M} | \psi_a \rangle & \langle \psi_a | \hat{M} | \psi_b \rangle & \cdots \\ \langle \psi_b | \hat{M} | \psi_a \rangle & \langle \psi_b | \hat{M} | \psi_b \rangle & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \quad (33)$$

## 0.5 $e^{\hat{M}}$ : Exponentiation of operators

It will be helpful to understand how to construct functions of operators, and a particularly important example is the exponential function,  $e^x$ . To decode what this means if the exponent is an operator, we can start with the Taylor series for the exponential function, which we'll take as its *definition*:

$$\begin{aligned} e^x &= \sum_{n=0}^{\infty} \frac{x^n}{n!} \\ &= 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24} + \cdots \end{aligned}$$



If we now replace the scalar  $x$  with some operator  $\hat{M}$ , we have

$$\begin{aligned}
e^{\hat{M}} &= \sum_{n=0}^{\infty} \frac{\hat{M}^n}{n!} \\
&= \hat{M}^0 + \hat{M} + \frac{\hat{M}^2}{2} + \frac{\hat{M}^3}{6} + \frac{\hat{M}^4}{24} + \dots \\
&= \mathbb{1} + \hat{M} + \frac{\hat{M}\hat{M}}{2} + \frac{\hat{M}\hat{M}\hat{M}}{6} + \frac{\hat{M}\hat{M}\hat{M}\hat{M}}{24} + \dots,
\end{aligned} \tag{34}$$

which shows that the exponential function of an operator is itself an operator.

A useful case of this is one in which the exponential function of an operator acts on an eigenvector of that operator. For example, if  $\hat{M}|m\rangle = m|m\rangle$ , then

$$\begin{aligned}
e^{\hat{M}}|m\rangle &= \left( \mathbb{1} + \hat{M} + \frac{\hat{M}\hat{M}}{2} + \frac{\hat{M}\hat{M}\hat{M}}{6} + \dots \right) |m\rangle \\
&= \left( \mathbb{1}|m\rangle + \hat{M}|m\rangle + \frac{\hat{M}\hat{M}}{2}|m\rangle + \frac{\hat{M}\hat{M}\hat{M}}{6}|m\rangle + \dots \right) \\
&= \left( |m\rangle + m|m\rangle + \frac{mm}{2}|m\rangle + \frac{mmm}{6}|m\rangle + \dots \right) \\
&= \left( 1 + m + \frac{m^2}{2} + \frac{m^3}{6} + \dots \right) |m\rangle \\
&= e^m |m\rangle.
\end{aligned} \tag{35}$$

Note that this replacement  $e^{\hat{M}}|\psi\rangle \rightarrow e^m|\psi\rangle$  *only* works if  $|\psi\rangle$  is an eigenvector of  $\hat{M}$  (with eigenvalue  $m$ ).

An important caveat to keep in mind is that the scalar algebra you are used to using with the exponential function may need to be modified when it is no longer a scalar due to the operator nature of the exponent. In particular, the scalar rule  $e^x e^y = e^y e^x = e^{x+y}$  is no longer true if  $x$  and  $y$  are replaced with general operators:

$$e^{\hat{M}} e^{\hat{N}} \neq e^{\hat{N}} e^{\hat{M}} \neq e^{\hat{M}+\hat{N}}. \tag{36}$$

It is only in the special case in which  $\hat{M}$  and  $\hat{N}$  commute (*viz.*  $[\hat{M}, \hat{N}] = 0$ ) that the above statements can be replaced with equalities.

