Outline

1. Real and complex p orbitals (and for any $\ell > 0$ orbital)

2. Dirac Notation :Symbolic vs shorthand
   Hilbert Space
   Vectors,

3. Theorems vs. Postulates

Scalar (inner) prod.

bra-ket = row-column

relation to integrals of functions

outer products operators

Complex H Wavefunctions

$$2s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{2a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right)e^{-Zr/2a}$$

$$2p_{-1} = \frac{1}{8\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\, e^{-i\phi}$$

$2p_{-1} = 2p_x - i2p_y$

$2p_1 = 2p_x + i2p_y$

Eigenfunctions of L_z operator

$L_z\,|2p_{-1}\rangle = -1\,|2p_{-1}\rangle$ m= -1

$L_z\,|2p_1\rangle = +1\,|2p_1\rangle$ m= +1

TABLE 6.2 Real Hydrogenlike Wave Functions

$$1s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$2s = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\,\cos\phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\sin\phi$$

$$3s = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}$$

$$3p_z = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\cos\theta$$

$$3p_x = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\cos\phi$$

$$3p_y = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\sin\phi$$

$$3d_{z^2} = \frac{1}{81(6\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}(3\cos^2\theta - 1)$$

$$3d_{xz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\cos\phi$$

$$3d_{yz} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\sin\phi$$

$$3d_{x^2-y^2} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\cos 2\phi$$

$$3d_{xy} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\sin 2\phi$$

$2p_{-1} = 2p_x - i2p_y$

$2p_1 = 2p_x + i2p_y$

Eigenfunctions of L_z operator

$L_z |2p_{-1}\rangle = -1 |2p_{-1}\rangle$ m= -1

$L_z |2p_1\rangle = +1 |2p_1\rangle$ ψψm= +1

$$\Psi_{2p_1} = R(r)\Theta(\theta)e^{im\phi}$$

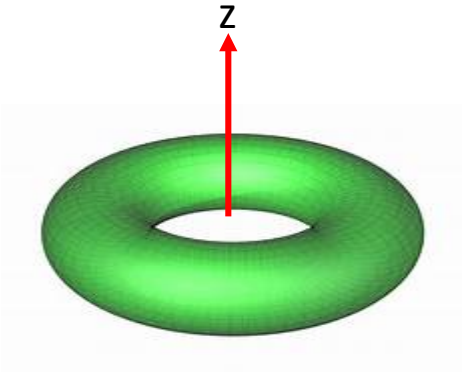
$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$L_z\Psi_{2p_1} = R(r)\Theta(\theta)(-i\hbar\frac{\partial\Psi_{2p1}}{\partial\phi}$$

$$L_z e^{im\phi} = -i\hbar\frac{\partial e^{im\phi}}{\partial\phi} = -i\hbar im\, e^{im\phi} = m\hbar e^{im\phi}$$

$$e^{im\phi} = \cos(m\phi) + i\sin(m\phi)$$

What does the orbital $2p_1$ look like?



Where is the anglular momentum?

The **time dependent Schrodinger Eq.** reveals a traveling wave of electron density moving around the z axis

$$e^{im\phi} = \cos(\phi) + i\sin(\phi)$$

$$e^{-im\phi} = \cos(\phi) - i\sin(\phi)$$

$$\cos(\phi) = \frac{e^{im\phi} + e^{-im\phi}}{2}$$

$$\sin(\phi) = \frac{e^{im\phi} - e^{-im\phi}}{2i}$$

2. Dirac Notation :Symbolic vs shorthand

   Hilbert Space

   Vectors, ...

The 3 body problem is not solvable in classical or QM.

Approximations, however, can be more accurate than experiment,
(given enough computer power and time)

Thus, we soon will start learning/reviewing the Variation Principle and methods, which are the foundation of computational quantum chemistry.

First: Briefly review underlying notations, theorems and postulates of QM Use Chapter 7 of Levine as guide--but interject quotations from Dirac;

Eq. (7.1) Levine: bracket notation introduced by Dirac:

$$\int f_m^* \hat{A} f_n \, d\tau \equiv \left\langle f_m \middle| \hat{A} \middle| f_n \right\rangle \equiv \left\langle m \middle| \hat{A} \middle| n \right\rangle \equiv A_{mn}$$ where A_{mn} is called a matrix element

But, on p 166 Levine states: "We will occasionally use a notation (called **ket** notation) in which an arbitrary function *f* is denoted by the symbol |*f*>. There doesn't seem to be any point to this notation, but in advance formulations of QM, it takes on a special significance."

Whereas Levine mostly considers this just shorthand, clearly **Dirac had a deeper meaning in mind:**

Quotes from Dirac preface, 1930 ("Reading 1")

... a book on the new physics, if not purely descriptive of experimental work, must be essentially mathematical. All the same the mathematics is only a tool and one should learn to hold the physical ideas in one's mind without reference to the mathematical form. In this book I have tried to keep the physics to the forefront,

... an author must decide at the outset between two methods. There is the symbolic method, which deals directly in an abstract way with the quantities of fundamental importance (the invariants, etc., of the transformations) and there is the method of coordinates or representations, which deals with sets of numbers corresponding to these quantities. The second of these has usually been used ...

bra and ket

wavefunctions and matrices

The symbolic method, however, seems to go more deeply into the nature of things. It enables one to express the physical laws in a neat and concise way, and will probably be increasingly used in the future as it becomes better understood and its own special mathematics gets

Paraphrased from Dirac:

Superposition principle suggests states are an infinite set of complex ***vectors*** which he named: ***kets , |>***

Then noted "Whenever we have a set of vectors in any mathematical theory, we can always set up another set of vectors ... the dual vectors... , which he called **bra** vectors, <|, and which together make ***brackets***.(ha ha)

We have the rules that ***any complete bracket expression denotes a number and any incomplete bracket expression denotes a vector of the bra or ket kind***.

We now make the assumption of one-to-one correspondence between the bras and kets, ... and the bra corresponding to c|A> is <A|c*

... any state of our dynamical system at a particular time may be specified by the direction of a bra vector just as well as by the direction of the ket..
...the whole theory will be ***symmetrical*** regarding bras and kets.

This was later recognized as a ***Hilbert space***

Lowdin later stated: "The mathematics of QM is that of **analytic geometry."**

Other notational statements by Levine $\langle m|n\rangle^* = \langle n|m\rangle$

$$\left\langle cf\left|\hat{B}\right|g\right\rangle = c^*\left\langle f\left|\hat{B}\right|g\right\rangle$$

$$\left\langle f\left|\hat{B}\right|c\,g\right\rangle = c\left\langle f\left|\hat{B}\right|g\right\rangle$$

Next: 9 Theorems and 5 Postulates

theorem: can be proved by chain of reasoning; a truth established by accepted truths.

postulate: accepted as true without proof.

7.2 Hermitian operators

$$\int \Psi^* \hat{A} \Psi \, d\tau = \langle A \rangle = \langle A \rangle^* \text{ for real (physical) operators}$$

For operators representing observable physical variables

One definition of Hermitian often seen is: $\int \Psi^* \hat{A} \Psi \, d\tau = \left[\int \Psi^* \hat{A} \Psi \, d\tau \right]^* = \int \Psi \left(\hat{A} \Psi \right)^* d\tau$

An other, seemingly more powerful, is: $\int f^* \hat{A} g \, d\tau = \int g \left(\hat{A} f \right)^* d\tau$

But Levine shows on page 157 that latter may be derived from from the first, and concludes that the **two forms are equivalent**.

Theorem 1. The eigenvalues of an Hermitian operator are real numbers

Theorem 2. The eigenfunctions of an Hermitian operator are orthogonal—unless the eigenvalues are degenerate. They can be made orthogonal, however

7.2 Hermitian operators

Hermitian means **"self-adjoint"**

What is **adjoint?** $\text{adjoint of } \hat{A} \equiv \hat{A}^{\dagger}$

Adjoint means: take the complex conjugate and **operate backwards**

$$\int f^{*} \hat{A}^{\dagger} g \, d\tau = \int g \hat{A}^{*} f^{*} d\tau$$

The adjoint operator does ***not*** generally give the same result as the original operator;

A **self-adjoint** operator **always** gives the **same** result as the original operator.

"The adjoint of an operator ***A*** may also be called the **Hermitian adjoint**, **Hermitian conjugate** or **Hermitian transpose"** https://en.wikipedia.org/wiki/Hermitian_adjoint

$$\int f^* \hat{A} g \, d\tau = \int f^* \hat{A}^\dagger g \, d\tau = \int g \hat{A}^* f^* d\tau = \int g \left(\hat{A} f \right)^* d\tau$$

In other words, one gets the same number whether using a certain operator or using its adjoint, which leads to the definition used on the previous on the previous page.

Other identities:

$$\left| n \right\rangle^\dagger = \left\langle n \right|$$

$$\left\langle m \middle| n \right\rangle^\dagger = \left\langle n \middle| m \right\rangle = \left\langle m \middle| n \right\rangle^*$$

$$\left\langle m \middle| \hat{A} \middle| n \right\rangle \equiv A_{mn}$$

$$\left\langle m \middle| \hat{A}^\dagger \middle| n \right\rangle = \left\langle n \middle| \hat{A}^* \middle| m \right\rangle = A_{mn} = A_{nm}^*$$

i.e., the definition of a **Hermitian matrix**

Math of QM = math of analytic geometry
(relation to row and column vectors)

ket = column vector bra = row vector

$$|a\rangle = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix}$$

$$\langle a| = \begin{bmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{bmatrix}$$

dot product = scalar product = inner product

$$\langle a|a\rangle = \begin{bmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = a_1^* a_1 + a_2^* a_2 + a_3^* a_3 + a_4^* a_4$$

a positive, real number

= 1 if $|a\rangle$ is normalized

$$\langle a|b\rangle = \begin{bmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} = a_1^* b_1 + a_2^* b_2 + a_3^* b_3 + a_4^* b_4$$

a real or complex number

= 0 if $|a\rangle$ and $|b\rangle$ are orthogonal

Matrices and Matrix Multiplication

row – column rule:

the row subscript is always FIRST e.g., a_{rc}

Matrix multiplication: $\mathbf{A} \bullet \mathbf{B} = \mathbf{C}$

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}$$

The result **C** of "multiplying" two matrices **A** and **B** is all possible **scalar products** of the **rows of A** with the **columns of B**. In other words:

$$C_{mn} = \sum_{k} A_{mk} B_{kn}$$

Non-square matrices may be multiplied, **but only if the number of columns of the left-hand matrix = the number of rows in the right-hand matrix**

For example a 4 row by 3 column matrix x a 3 row, 2 column matrix
(4 by 3 x 3 by 2) yields a 4 row by 2 column matrix

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \\ a_{41} & a_{42} & a_{43} \end{bmatrix} \times \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \\ b_{31} & b_{32} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \\ c_{31} & c_{32} \\ c_{41} & c_{42} \end{bmatrix}$$

A scalar product of different non-orthogonal vectors:

$$\langle a|b\rangle = \begin{bmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} = a_1^* b_1 + a_2^* b_2 + a_3^* b_3 + a_4^* b_4$$

a number

is a 1 by 4 matrix multiplying a 4 by 1 matrix = a 1 by 1 matrix = **a number**

Outer Products

Outer Product = |b><a| = Operator

Operators ***change*** the "direction" and magnitude of bras and kets

$$\text{let } \langle a| \langle b| \text{ be normalized and orthogonal:}$$

$$|b\rangle\langle a| \text{ operating on } |a\rangle = |b\rangle\langle a|a\rangle = |b\rangle$$

$$|a\rangle\langle b| \text{ operating on } |a\rangle = |a\rangle\langle a|b\rangle = 0$$

|b><a| = column vector x row vector

$|b\rangle\langle a|$ = column vector x row vector

$$|b\rangle\langle a| = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} \begin{bmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{bmatrix} =$$

a 4 by 1 matrix times a 1 by 4 matrix

= a 4 by 4 "matrix"

$$|b\rangle\langle a|a\rangle = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} \begin{bmatrix} a_1^* & a_2^* & a_3^* & a_4^* \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} = |b\rangle$$

$$|a\rangle\langle b|a\rangle = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \begin{bmatrix} b_1^* & b_2^* & b_3^* & b_4^* \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = 0$$

$$|a\rangle\langle b|a\rangle = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} \begin{bmatrix} b_1^* & b_2^* & b_3^* & b_4^* \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = 0$$

$$|a\rangle\langle b|c\rangle = \begin{bmatrix} a_1 b_1^* & a_1 b_2^* & a_1 b_3^* & a_1 b_4^* \\ a_2 b_1^* & a_2 b_2^* & a_2 b_3^* & a_2 b_4^* \\ a_3 b_1^* & a_3 b_2^* & a_3 b_3^* & a_3 b_4^* \\ a_4 b_1^* & a_4 b_2^* & a_4 b_3^* & a_4 b_4^* \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{bmatrix} = \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ d_4 \end{bmatrix}$$

$$d_i = \sum_j a_i b_j c_j$$

Relation between wavefunctions and vectors:

In the previous lecture we noted that:

$$\int \Psi_m^*(x)\Psi_n(x)dx \equiv \left\langle \Psi_m \middle| \Psi_n \right\rangle \equiv \left\langle m \middle| n \right\rangle \equiv A_{mn}$$

which clearly means that the common "overlap" integral on the left must be an ***inner product*** of two vectors.

In what sense is can we think of the integral as the scalar product of two vectors when we are used to thinking of the wavefunctions in the integral as common functions of x?

Before giving a formal answer in terms of the Dirac delta function, one can simply recall the definition of acceptable quantum mechanical state functions, for which at every point in space there exists a single complex number, the absolute square of which is proportional to probability density for finding the particle. This is **Postulate 1** of quantum mechanics in most text books.

Imagine, now, ***infinitely*** long column and row vectors in which are stored all the numbers which are the values of $\Psi(x)$ and $\Psi^*(x)$, respectively at all possible values of x.

Thus, all integrals in this notation are actually just scalar products of two vectors. They are formally infinite because in calculus the result is only exactly correct in the limit of $dx \rightarrow 0$. In all actual calculations of numbers, on computers, dx is a very small—but finite—Δx. This truly turns the function into a vector of numbers, as large as we care to make by using smaller values of Δx and larger range of x. This is fine, because the human mind cannot grasp infinitesimal and infinity, and **we always use finite vectors in calculations**.

This idea is true for any number of coordinates, of course.