Chapter 2

Mathematical Formulation of the Superposition Principle

Superposition $\longrightarrow$ add states together, get new states.

Math quantity associated with states must also have this property.

Vectors have this property.

In real three dimensional space, three basis vectors are sufficient to describe any point in space.

Can combine three vectors to get new bases vectors, which are also O.K. under appropriate combination rules.

In Q. M., may have many more than three states.

Need one vector for each state.

May be finite or infinite number of vectors; depends on finite or infinite number of states of the system.

Dirac $\rightarrow$ Call Q.M. vectors ket vectors or just kets.

Symbol $\rightarrow$ $| \ \rangle$ general ket

Particular ket, A $\rightarrow$ $|A\rangle$

Kets can be multiplied by complex numbers and added.

$$|R\rangle = C_1 |A\rangle + C_2 |B\rangle$$

complex numbers

Can add together any number of kets. $|S\rangle = \sum_i C_i |L_i\rangle$ Vector space

If $|x\rangle$ is continuous over some range of x

$$|Q\rangle = \int C(x) |x\rangle dx$$

Hilbert space

Dependent and Independent Kets

A ket that is expressible linearly in terms of other kets is *dependent* on them.

$$|R\rangle = C_1|A\rangle + C_2|B\rangle$$

$|R\rangle$ is dependent on $|A\rangle$ and $|B\rangle$

A set of kets is *independent* if no one of them is expressible linearly in terms of the others.

(In real space, three orthogonal basis vectors are independent.)

Connection between theory and real world

Assume: **Each state of a dynamical system at a particular time corresponds to a ket vector, the correspondence being such that if a state results from a superposition of other states, its corresponding ket vector is expressible linearly in terms of the corresponding ket vectors of the other states.**

Order of superposition doesn't matter.

$$|R\rangle = C_1|A\rangle + C_2|B\rangle = C_2|B\rangle + C_1|A\rangle$$

If $|R\rangle = C_1|A\rangle + C_2|B\rangle$,

then, $|A\rangle$ **can be expressed in terms of** $|R\rangle$ **and** $|B\rangle$ **, etc.**

$$|A\rangle = b_1|B\rangle + b_2|R\rangle$$

A state is dependent on other states if its ket is dependent on the corresponding kets of the other states.

The superposition of a state with itself is the same state.

$$C_1|A\rangle + C_2|A\rangle = (C_1 + C_2)|A\rangle \Rightarrow |A\rangle$$

unless $(C_1 + C_2) = 0$ then no state.

A ket corresponding to a state multiplied by any complex number (other than 0) gives a ket corresponding to the same state.

State corresponds to direction of ket vector.

The length is irrelevant.

The sign is irrelevant.

$|R\rangle \Rightarrow$ some state

$C|R\rangle = |R\rangle$ same state (Unless $C = 0$)

Ket $|A\rangle$ number φ

φ is a linear function of $|A\rangle$

If

$$|A\rangle \Rightarrow \varphi \quad \text{and} \quad |A'\rangle \Rightarrow \varphi'$$

then

$$|A\rangle + |A'\rangle \Rightarrow \varphi + \varphi'$$

and

$$C|A\rangle \Rightarrow C\varphi$$

To get a number that is a linear function of a vector, take the scalar product with some other vector.

Other vector $\longrightarrow$ **Bra**

symbol $\langle \quad |$

particular one $\langle \boldsymbol{B} |$

Put a bra and a ket together $\langle \boldsymbol{bra} | \boldsymbol{ket} \rangle \Rightarrow$ **bracket**

Any complete bracket $\langle \quad | \quad \rangle \Rightarrow$ **number**

Incomplete bracket $\Rightarrow$ **vector**

$| \quad \rangle$ **ket vector**

$\langle \quad |$ **bra vector**

$\langle \quad | \quad \rangle \Rightarrow$ **scalar product, a complex number**

$$\langle B|\{|A\rangle+|A'\rangle\}=\langle B|A\rangle+\langle B|A'\rangle$$

Scalar product with sum of kets.

$$\langle B|\{C|A\rangle\}=C\langle B|A\rangle$$

Scalar product with constant times ket.

Bra completely defined when its scalar product with every ket is known.

If $\langle \mathrm{P}|\mathrm{A}\rangle = 0$ **for all** $|\mathrm{A}\rangle \Rightarrow \langle P| = 0$

Addition of bras defined by scalar product with ket $|A\rangle$**.**

$$\{\langle B|+\langle B'|\}|A\rangle=\langle B|A\rangle+\langle B'|A\rangle$$

Multiplication of bra by a constant defined by scalar product with ket $|A\rangle$ **.**

$$\{C\langle B|\}|A\rangle=C\langle B|A\rangle$$

Assume: There is a one to one correspondence between kets and bras such that the bra corresponding to $|A\rangle + |A'\rangle$ is the sum of the bras corresponding to $|A\rangle$ and $|A'\rangle$ and that the bra corresponding to $C|A\rangle$ is $\bar{C}$ or C^* times the bra corresponding to $|A\rangle$.

$\bar{C}$ or C^* is the complex conjugate of the complex number C.

Bra is the complex conjugate of Ket.

$$\langle A| = \overline{|A\rangle}$$

Theory symmetrical in kets and bras. State of a system can be specified by the direction of a bra as well as a ket.

Since

$$\langle A| = \overline{|A\rangle} \qquad \textbf{and}$$

$$\langle B| = \overline{|B\rangle}$$

then

$$\langle B|A\rangle = \overline{\langle A|B\rangle}$$

The complex conjugate of a bracket is the bracket in "reverse order."

For $|B\rangle = |A\rangle$

$$\langle A|A\rangle = \overline{\langle A|A\rangle}$$

$\Rightarrow \langle A|A\rangle$ **is a real number because a number equal to its complex conjugate is real.**

Assume $\langle A|A\rangle > 0$ **Length of a vector is positive unless** $|A\rangle = 0$

$$\left(\langle A|A\rangle\right)^{1/2} = \text{ length of vector}$$

Scalar Product

Real space vectors – scalar product gives a real number;
symmetrical with respect to interchange of order.

$$\vec{\mathbf{A}} \cdot \vec{\mathbf{B}} = \vec{\mathbf{B}} \cdot \vec{\mathbf{A}}$$

Kets and Bras – scalar product gives complex number.

$$\langle A | B \rangle = \overline{\langle B | A \rangle}$$

Interchange of order gives complex conjugate number.

Orthogonality

Bra and Ket orthogonal if $\langle B | A \rangle = 0$ scalar product equals zero.

2 Bras or 2 Kets orthogonal;

$|B\rangle$ and $|A\rangle$ orthogonal if

$$\langle B | A \rangle = 0$$

$\langle B|$ and $\langle A|$ orthogonal if

$$\langle B | A \rangle = 0$$

Two states of a dynamical system are orthogonal if the vectors representing them are orthogonal.

Normalization of Bras and Kets

Length of $\langle A|$ or $|A\rangle$ is

$$\left(\langle A|A\rangle\right)^{1/2}$$

Length doesn't matter, only direction.

May be convenient to have

$$\left(\langle A|A\rangle\right)^{1/2} = 1$$

If this is done $\Rightarrow$ States are normalized.

Normalized ket still not completely specified

A ket is a vector – direction
Normalized ket – direction and length

But, can multiply by $\mathrm{e}^{i\gamma}$ γ a real number

$$\left(\langle A|A\rangle\right)^{1/2} = 1$$ normalized ket

$$|A'\rangle = e^{i\gamma}|A\rangle$$ multiply by $\mathrm{e}^{i\gamma}$

$$\langle A'| = e^{-i\gamma}\langle A|$$ complex conjugate of $|A'\rangle$

$$\left(\langle A'|A'\rangle\right)^{1/2} = \left[e^{-i\gamma}e^{i\gamma}\langle A|A\rangle\right]^{1/2} = 1$$ still normalized

$\mathrm{e}^{i\gamma}$ with γ real called a "phase factor." Very important. See later.

State of system defined by direction of ket, not length.

Linear Operators

Kets and bras represent states of a dynamical system, s, p, d, etc states of H atom.
Need math relations to work with ket vectors to obtain observables.

Ket $|F\rangle$ **is a function of ket** $|A\rangle$

$$|F\rangle = \underline{\alpha}\,|A\rangle$$

$\underline{\alpha}$ **is a linear operator.** **(Underline operator to indicate it is an operator)**
Linear operators have the properties:

$$\underline{\alpha}\left(|A\rangle + |A'\rangle\right) = \underline{\alpha}\,|A\rangle + \underline{\alpha}\,|A'\rangle$$

$$\underline{\alpha}\left(c\,|A\rangle\right) = c\,\underline{\alpha}\,|A\rangle$$

complex number

A linear operator is completely defined when its application to every ket is known.

Rules about linear operators

Additive

$$\{\underline{\alpha}+\underline{\beta}\}\left|A\right\rangle=\underline{\alpha}\left|A\right\rangle+\underline{\beta}\left|A\right\rangle$$

Multiplication - associative

$$\{\underline{\alpha}\,\underline{\beta}\}\left|A\right\rangle=\underline{\alpha}\{\underline{\beta}\left|A\right\rangle\}=\underline{\alpha}\,\underline{\beta}\left|A\right\rangle$$

Multiplication is <u>NOT</u> necessarily commutative

$$\underline{\alpha}\,\underline{\beta}\left|A\right\rangle\neq\underline{\beta}\,\underline{\alpha}\left|A\right\rangle$$ **in general**

If $\underline{\gamma}\,\underline{\delta} = \underline{\delta}\,\underline{\gamma}$

then $\underline{\gamma}$ and $\underline{\delta}$ commute.

Only know what an operator does by operating on a ket.

$\underline{\gamma}\,\underline{\delta} = \underline{\delta}\,\underline{\gamma}$ really means

$$\underline{\gamma}\,\underline{\delta}\left|A\right\rangle = \underline{\delta}\,\underline{\gamma}\left|A\right\rangle$$

$\underline{\gamma}\,\underline{\delta} = \underline{\delta}\,\underline{\gamma}$ is a short hand. It does not mean the right and left hand sides of the equation are equal algebraically.

It means $\underline{\gamma}\,\underline{\delta}$ and $\underline{\delta}\,\underline{\gamma}$ have the same result when applied to an arbitrary ket.

Put ket on right of linear operator.

$$\underline{\alpha}\left|A\right\rangle = \left|F\right\rangle$$

Bras and linear operators

$$\left\langle Q\right| = \left\langle B\right|\underline{\gamma}$$

Put bra on left of linear operator.

$$\left\langle B\right|\left\{\underline{\alpha}\left|A\right\rangle\right\} = \left\langle B\right|\underline{\alpha}\left|A\right\rangle$$

This is a number. It is a closed bracket $\longrightarrow$ number.

To see this consider

$$\left\langle B\right|\underline{\alpha}\left|A\right\rangle = \left\langle B\right|\left\{\underline{\alpha}\left|A\right\rangle\right\}$$

$$= \left\langle B\middle|Q\right\rangle = c$$

a complex number

Kets and Bras as linear operators

$\langle A|B\rangle$ is a number

but

$|A\rangle\langle B|$ is a linear operator.

not closed bracket

Operate on an arbitrary ket $|P\rangle$

$$|A\rangle\langle B|P\rangle = |A\rangle\varphi$$

a number

$$= \varphi|A\rangle$$

Operating on $|P\rangle$ gave $|A\rangle$, a new ket. Therefore, $|A\rangle\langle B|$ is an operator.

Can also operate on a bra $\langle Q|$.

$$\langle Q|A\rangle\langle B| = \theta\langle B|$$

new bra

Will use later; projection operators

Have algebra involving bras, kets and linear operators.

1. **associative law of multiplication holds**

2. **distributive law holds**

3. **commutative law does not hold**

4. $\langle \;\; \rangle \Rightarrow$ **number**

5. $| \;\; \rangle$ **or** $\langle \;\; | \Rightarrow$ **vector**

Assume: The linear operators correspond to the dynamical variables of a physical system.

Dynamical Variables

coordinates
components of velocity
momentum
angular momentum
energy
etc.

Linear Operators $\Rightarrow$ Questions you can ask about a system.

For every experimental observable, there is a linear operator.

Q. M. dynamical variables not subject to an algebra in which the commutative law of multiplication holds.

Consequence of Superposition Principle.
(Will lead to the Uncertainty Principle.)

Conjugate relations

Already saw that $\langle B|A\rangle = \overline{\langle A|B\rangle}$ Complex conjugate – reverse order

With linear operators

$$\langle B|\bar{\underline{\alpha}}|P\rangle = \overline{\langle P|\underline{\alpha}|B\rangle}$$

$\bar{\underline{\alpha}} \longrightarrow$ complex conjugate of the operator $\underline{\alpha}$.

$\bar{\bar{\underline{\alpha}}} = \underline{\alpha} \longrightarrow$ complex conjugate of complex conjugate

If $\bar{\underline{\alpha}} = \underline{\alpha}$, the operator is "self-adjoint."
It corresponds to a real dynamical variable.

$\bar{\underline{\alpha}} = \underline{\alpha}$ means $\bar{\underline{\alpha}}|Q\rangle = \underline{\alpha}|Q\rangle$ all $|Q\rangle$

$$\overline{\underline{\beta}}\;\overline{\underline{\alpha}} = \overline{\underline{\alpha}\;\underline{\beta}}$$

$$\overline{\underline{\alpha}\;\underline{\beta}\;\underline{\gamma}} = \overline{\underline{\gamma}}\;\overline{\underline{\beta}}\;\overline{\underline{\alpha}}$$

$$\overline{\left|A\right\rangle\left\langle B\right|} = \left|B\right\rangle\left\langle A\right|$$

The complex conjugate of any product of bras, kets, and linear operators is the complex conjugate of each factor with factors in reverse order.

Eigenvalues and Eigenvectors

$$\underline{\alpha}\left|P\right\rangle = p\left|P\right\rangle$$

linear operator   ket   number (real)   same ket

Eigenvalue problem (Mathematical problem in linear algebra.)

Know $\underline{\alpha}$.
want to find $\left|P\right\rangle$ and p.

eigenvector   eigenvalue

Apply linear operator to ket, get same ket back multiplied by a number.

Can also have $\left\langle Q\right|\underline{\alpha} = q\left\langle Q\right|$

$\left\langle Q\right|$ is an eigenbra of $\underline{\alpha}$.

Observables and Linear Operators

Kets (or bras) $\Rightarrow$ **State of dynamical system.**

Linear operators $\Rightarrow$ **Dynamical variables.**
Questions you can ask about the state of a system.

Observables $\Rightarrow$ **Real Dynamical Variables.**

Observables are the eigenvalues of Hermitian Linear Operators.

Hermitian operators $\rightarrow$ **Real Dynamical Variables.**

Hermitian operator

$$\langle a | \underline{\gamma} | b \rangle = \langle a | \overline{\underline{\gamma}} | b \rangle$$

If $|b\rangle = |a\rangle$

$$\langle a | \overline{\underline{\gamma}} | a \rangle = \langle a | \underline{\gamma} | a \rangle$$

Observables $\Rightarrow$

Eigenvalues of Hermitian Operators (real eigenvalues)

$$\underline{\alpha}\left|P\right\rangle = p\left|P\right\rangle$$

linear operator

observable value

eigenvector
eigenket

For every observable there is a linear operator

(more than one form, different representations of QM).

The eigenvalues are the numbers you will measure

in an experiment.

Some important theorems and proofs

If an eigenvector of $\underline{\alpha}$ is multiplied by any number C other than zero,

then the product is still an eigenvector with the same eigenvalue.

(Length doesn't matter, only direction.)

$$\underline{\alpha}\left|A\right\rangle = a\left|A\right\rangle$$

$$\underline{\alpha}\,[C\left|A\right\rangle] = C\,[\underline{\alpha}\left|A\right\rangle] \longleftarrow$$

A constant commutes with an operator. A constant can be thought of as a number times the identity operator. The identity operator commutes with any other operator.

$$= C[a\left|A\right\rangle]$$

$$= a[C\left|A\right\rangle]$$

This is the reason that the direction, not the length, of a vector describes the state of a system. Eigenvalues (observable values) not changed by length of vector as long as $C \neq 0$.

Several independent eigenkets of an operator $\underline{\alpha}$ can have the same eigenvalues. $\longrightarrow$ **Degenerate**

Any superposition of these eigenkets is an eigenket with the same eigenvalue.

$$\underline{\alpha}\left|P_1\right\rangle = p\left|P_1\right\rangle$$

$$\underline{\alpha}\left|P_2\right\rangle = p\left|P_2\right\rangle$$

$$\underline{\alpha}\left|P_3\right\rangle = p\left|P_3\right\rangle$$

$$\underline{\alpha}\left\{C_1\left|P_1\right\rangle + C_2\left|P_2\right\rangle + C_3\left|P_3\right\rangle\right\} = C_1\underline{\alpha}\left|P_1\right\rangle + C_2\underline{\alpha}\left|P_2\right\rangle + C_3\underline{\alpha}\left|P_3\right\rangle$$

$$= p\left\{C_1\left|P_1\right\rangle + C_2\left|P_2\right\rangle + C_3\left|P_3\right\rangle\right\}$$

Example: p_x, p_y, and p_z orbitals of the H atom.

The eigenvalues associated with the eigenkets are the same as those for the eigenbras for the same linear operator.

Assume not the same.

$$\underline{\gamma}\,|P\rangle = a\,|P\rangle$$

$$\langle P|\,\underline{\gamma} = b\,\langle P| \qquad \overline{\underline{\gamma}} = \underline{\gamma} \qquad \text{Hermitian property}$$

Left multiply top by $\langle P|$

Right multiply bottom by $|P\rangle$

$$\langle P|\underline{\gamma}|P\rangle = a\langle P|P\rangle$$

$$\langle P|\underline{\gamma}|P\rangle = b\langle P|P\rangle$$

Subtract

$$0 = (a-b)\langle P|P\rangle$$

But, $\langle P|P\rangle > 0$

Therefore, a = b

Theory is symmetrical in kets and bras.

The eigenvalues of Hermitian operators are real.

$$\underline{\gamma} \left| P \right\rangle = a \left| P \right\rangle$$

take complex conjugate

$$\left\langle P \right| \underline{\bar{\gamma}} = \left\langle P \right| \bar{a}$$

$$\left\langle P \right| \underline{\gamma} = \left\langle P \right| \bar{a}$$

Hermitian property

Left multiply the first equation by $\left\langle P \right|$

Right multiply third equation by $\left| P \right\rangle$

$$\left\langle P \right| \underline{\gamma} \left| P \right\rangle = a \left\langle P | P \right\rangle$$

$$\left\langle P \right| \underline{\gamma} \left| P \right\rangle = \bar{a} \left\langle P | P \right\rangle$$

Subtract

$$0 = (a - \bar{a}) \left\langle P | P \right\rangle$$

$$\left\langle P | P \right\rangle > 0$$

Length of vector greater than zero.

Therefore, $\bar{a} = a$; and a number equal to its complex conjugate is real.

Observables are real numbers.

The Orthogonality Theorem

Two eigenvectors of a real dynamical variable (Hermitian operator - observable) belonging to different eigenvalues are orthogonal.

$$\underline{\gamma}\left|\gamma'\right\rangle = \gamma'\left|\gamma'\right\rangle \qquad \textbf{(1)}$$

$$\underline{\gamma}\left|\gamma''\right\rangle = \gamma''\left|\gamma''\right\rangle \qquad \textbf{(2)}$$

Take complex conjugate of (1).

$$\left\langle\gamma'\right|\underline{\gamma} = \left\langle\gamma'\right|\gamma' \longleftarrow$$ **Operator Hermitian; eigenvalue real**

$$\left\langle\gamma'\right|\underline{\gamma}\left|\gamma''\right\rangle = \gamma'\left\langle\gamma'\middle|\gamma''\right\rangle \quad \textbf{(3)}$$ **Right multiply by** $\left|\gamma''\right\rangle$

$$\left\langle\gamma'\right|\underline{\gamma}\left|\gamma''\right\rangle = \gamma''\left\langle\gamma'\middle|\gamma''\right\rangle \quad \textbf{(4)}$$ **Left multiply (2) by** $\left\langle\gamma'\right|$

$$\mathbf{0} = (\gamma' - \gamma'')\left\langle\gamma'\middle|\gamma''\right\rangle$$ **Subtract (4) from (3)**

But $\gamma' \neq \gamma''$ **different eigenvalues**

Therefore, $\left\langle\gamma'\middle|\gamma''\right\rangle = \mathbf{0}$

$\left|\gamma'\right\rangle$ **and** $\left|\gamma''\right\rangle$ **are orthogonal.**