

Notes of Quantum Mechanics

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Preface

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Chapter 1

Mathematical Formalism

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1.1 Introduction

The formalism of quantum mechanics (QM) involves symbols and methods for denoting and determining the time dependent state of a physical system along with a mathematical structure for evaluating the possible outcomes and associated probabilities of measurements.

State

A **state** is everything knowable about the dynamical aspects of a system at a certain time.

A particle has associated a **wavefunction** $\psi(\mathbf{r}, t)$ whose probability interpretation resides on $|\psi(\mathbf{r}, t)|^2$: it represents the probability density function which serves as a probability finder in space and time. The probability of finding the particle somewhere in space is thus equal to 1:

$$\int_{\text{all space}} d^3r |\psi(\mathbf{r}, t)|^2 = 1. \quad (1.1)$$

Thus, in order that this integral converges, we must deal with a set of square-integrable functions, called L^2 . We can only retain the functions $\psi(\mathbf{r}, t)$ which are everywhere defined, continuous, and infinitely differentiable C^∞ . Also, we confine to wavefunctions that have a bounded domain (we can find the particle in a finite region of space).

We list the formal definition of a vector space which is used to define particular vector spaces.

Vector space

A **vector space** over a field F (set defined with addition and multiplication) is a non-empty set V together with a *vector addition* and a *scalar multiplication* that satisfies eight axioms. The elements of V are called vectors and the elements of F are called scalars.

| | | |
|---|---|-------|
| Commutativity of vector addition | $\mathbf{u} + \mathbf{v} = \mathbf{v} + \mathbf{u}$ | |
| Associativity of vector addition | $(\mathbf{u} + \mathbf{v}) + \mathbf{w} = \mathbf{u} + (\mathbf{v} + \mathbf{w})$ | |
| Identity element of vector addition | $\exists \mathbf{0}, \mathbf{v} \in V : \mathbf{v} + \mathbf{0} = \mathbf{v}$ | |
| Inverse element of vector addition | $\forall \mathbf{v} \in V, \exists -\mathbf{v} \in V : \mathbf{v} + (-\mathbf{v}) = \mathbf{0}$ | (1.2) |
| Associativity of scalar multiplication | $\alpha(\beta\mathbf{v}) = (\alpha\beta)\mathbf{v}$ | |
| Distributivity over vector addition | $\alpha(\mathbf{u} + \mathbf{v}) = \alpha\mathbf{u} + \alpha\mathbf{v}$ | |
| Distributivity over scalar addition | $(\alpha + \beta)\mathbf{v} = \alpha\mathbf{v} + \beta\mathbf{v}$ | |
| Identity element of scalar multiplication | $1\mathbf{v} = \mathbf{v}$ | |

When the scalar field is the real numbers, the vector space is called a real vector space, when the scalar field is the complex numbers, then is called a complex vector space.

Vector space \mathcal{F}

The set of wavefunctions $\mathcal{F} \in L^2$ is composed of sufficiently regular functions of L^2 .

1.1.1 Scalar product

With each pair of ordered elements of \mathcal{F} , $(\varphi(\mathbf{r}), \psi(\mathbf{r}))$, we associate a *complex number*:

$$(\varphi, \psi) = \int d^3r \varphi^*(\mathbf{r})\psi(\mathbf{r}) \in \mathbb{C}. \quad (1.3)$$

Its properties are listed below:

| | | |
|---------------------------------------|--|---|
| Adjoint | Linear in the second term | Antilinear in the first term |
| $(\varphi, \psi) = (\psi, \varphi)^*$ | $(\varphi, \lambda_1 \psi_1 + \lambda_2 \psi_2) = \lambda_1 (\varphi, \psi_1) + \lambda_2 (\varphi, \psi_2)$ | $(\lambda_1 \varphi_1 + \lambda_2 \varphi_2, \psi) = \lambda_1^* (\varphi_2, \psi) + \lambda_2^* (\varphi_2, \psi)$ |

If $(\varphi, \psi) = 0$, then $\varphi(\mathbf{r})$ and $\psi(\mathbf{r})$ are said to be **orthogonal**. In addition, the scalar product of a vector with itself return its *norm squared*:

$$\text{Parseval's theorem} \quad (\varphi, \varphi) = \int d^3r |\psi(\mathbf{r})|^2 \geq 0 \in \mathbb{R}. \quad (1.4)$$

We also have the Schwarz inequality defined with the norms:

$$|(\psi_1, \psi_2)| \leq \sqrt{(\psi_1, \psi_1)} \sqrt{(\psi_2, \psi_2)}. \quad (1.5)$$

1.1.2 Linear operators

A linear operator A is a mathematical entity which associates with every function $\phi(\mathbf{r}) \in \mathcal{F}$ another function $\phi'(\mathbf{r})$ linearly:

$$\begin{aligned} \phi'(\mathbf{r}) &= A\phi(\mathbf{r}) \\ A[\lambda_1 \phi_1(\mathbf{r}) + \lambda_2 \phi_2(\mathbf{r})] &= \lambda_1 A\phi_1(\mathbf{r}) + \lambda_2 A\phi_2(\mathbf{r}) \end{aligned} \quad (1.6)$$

Let A, B be two linear operators, their product AB on a vector corresponds to the application of B first, and then A acts on the new vector $\varphi(\mathbf{r}) = B\psi(\mathbf{r})$:

$$(AB)\psi(\mathbf{r}) = A[B\psi(\mathbf{r})]. \quad (1.7)$$

In general, the order of application matter and a way to quantify it is through the **commutator**:

$$[A, B] = AB - BA. \quad (1.8)$$

1.1.3 Discrete orthonormal bases in $\mathcal{F} : \{u_i(\mathbf{r})\}$

Definition of discrete orthonormal bases

Let be a countable set of function $\{u_1(\mathbf{r})\} \in \mathcal{F}$.

- This set is orthonormal if only the inner product of the same function returns a non-zero value:

$$\text{Orthonormalization relation} \quad (u_i, u_j) = \int d^3r u_i^*(\mathbf{r}) u_j(\mathbf{r}) = \delta_{ij}, \quad (1.9)$$

where δ_{ij} is the kronecker function:

$$\delta_{ij} = \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases}. \quad (1.10)$$

- It constitutes a **basis** if every function $\psi(\mathbf{r}) \in \mathcal{F}$ can be expanded in only **one way** in $\{u_i(\mathbf{r})\}$ as a linear combination:

$$\text{Expansion} \quad \psi(\mathbf{r}) = \sum_i c_i u_i(\mathbf{r}), \quad (1.11)$$

whose elements of projection c_i are obtained computing the scalar product $(u_j, \psi(x))$:

$$(u_j, \psi) = \left(u_j, \sum_i c_i u_i(\mathbf{r}) \right) = \sum_i c_i (u_j, u_i) = \sum_i c_i \delta_{ij} = c_j.$$

Thus,

$$\text{Coefficient expansion} \quad c_i = (u_i, \psi) = \int d^3r \, u_i^*(\mathbf{r}) \psi(\mathbf{r}). \quad (1.12)$$

Once projected in $\{u_i(\mathbf{r})\}$ it is equivalent to specify $\psi(\mathbf{r})$ or the set of c_i , which represent $\psi(\mathbf{r})$ in the $\{u_i(\mathbf{r})\}$ basis. The 3D generalization is given in A-22-A-24.

The scalar product of two wavefunctions can also be expressed in terms of the coefficients of projection. Let be $\varphi(\mathbf{r}), \psi(\mathbf{r})$,

$$(\varphi, \psi) = \left[\sum_i b_i u_i, \sum_j c_j u_j \right] = \sum_{i,j} b_i^* c_j (u_i, u_j) = \sum_{i,j} b_i^* c_j \delta_{ij}. \quad (1.13)$$

Therefore, the scalar product is:

$$\text{Scalar product} \quad (\varphi, \psi) = \sum_i b_i^* c_i \quad (1.14)$$

Its generalization for 3D is given in A-28.

Closure relation

Equation (1.9) is called *orthonormalization relation* over the set $\{u_i(\mathbf{r})\}$. There is another condition called *Closure relation*, which express the fact that this set constitutes a basis.

If $\{u_i(\mathbf{r})\} \in \mathcal{F}$, the any function $\psi(\mathbf{r}) \in \mathcal{F}$ is decomposed using equation (1.11):

$$\psi(\mathbf{r}) = \sum_i c_i u_i(\mathbf{r}) = \sum_i (u_i, \psi) u_i(\mathbf{r}) = \sum_i \left[\int d^3r' \, u_i^*(\mathbf{r}') \psi(\mathbf{r}') \right] u_i(\mathbf{r}) = \int d^3r' \, \psi(\mathbf{r}') \left[\sum_i u_i(\mathbf{r}) u_i^*(\mathbf{r}') \right]$$

This integration with sum will be $\psi(\mathbf{r})$ only when $\mathbf{r} = \mathbf{r}'$, which is characteristic of a delta function centered at $\mathbf{r} = \mathbf{r}'$. Thus, the only way to achieve that is that the sum must be a delta function $\delta(\mathbf{r} - \mathbf{r}')$ and we have

$$\text{Closure relation} \quad \sum_i u_i(\mathbf{r}) u_i^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (1.15)$$

If an orthonormal set $\{u_i(\mathbf{r})\}$ satisfies the closure relation then it constitutes a basis.

1.1.4 Bases not belonging to \mathcal{F}

The $\{u_i(\mathbf{r})\}$ bases are composed of square-integrable functions. It can also be convenient to introduce bases of functions **not belonging** to \mathcal{F} or L_2 , but in terms of which any wavefunction $\psi(\mathbf{r})$ can nevertheless be expanded. We will discuss two examples: 1D plane wave, and delta functions, after which we will study continuous bases.

Plane waves

Consider a plane wave $v_p(x)$ with wave vector p/\hbar

$$v_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}. \quad (1.16)$$

The integral of $|v_p(x)|^2 = \frac{1}{2\pi\hbar}$ over $x \in \mathbb{R}$ diverges, therefore $v_p(x) \notin \mathcal{F}_x$. We shall designate $\{v_o(x)\}$ the set of all plane waves, with the continuous index $p \in (-\infty, \infty)$. The Fourier-pair equations

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dp \bar{\psi}(p) e^{ipx/\hbar}, \quad \text{and} \quad \bar{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx \psi(x) e^{-ipx/\hbar},$$

can be rewritten with the definition of the plane wave:

$$\psi(x) = \int_{-\infty}^{\infty} dp \bar{\psi}(p) v_p(x), \quad (1.17)$$

$$\bar{\psi}(p) = (v_p, \psi) = \int_{-\infty}^{\infty} dx v_p^*(x) \psi(x). \quad (1.18)$$

The two formulas can be compared to equations (1.11) and (1.12). In this case, every function $\psi(x) \in \mathcal{F}_x$ can be expanded in only one way as a continuous linear combination of planes waves, whose components are given by (1.18). The set of these components constitutes a function of p , $\bar{\psi}(p)$, the Fourier transform of $\psi(x)$.

$\bar{\psi}(p)$ is analogous to c_i , both represent the components of the same function $\psi(x)$ in two different bases: $\{v_p(x)\}$ and $\{u_i(x)\}$.

If we calculate the square of the norm of $\psi(x)$ we will get:

$$\text{Parseval's theorem} \quad (\psi, \psi) = \int_{-\infty}^{\infty} dp |\bar{\psi}(p)|^2. \quad (1.19)$$

We can also show that $v_p(x)$ satisfy the closure relation:

$$\begin{aligned} \psi(x) &= \int_{-\infty}^{\infty} dp \bar{\psi}(p) v_p(x) = \int_{-\infty}^{\infty} dp (v_p, \psi) v_p(x) = \int_{-\infty}^{\infty} dp \left[\int_{-\infty}^{\infty} dx' v_p^*(x') \psi(x') \right] v_p(x) \\ &= \int_{-\infty}^{\infty} dx' \psi(x') \left[\int_{-\infty}^{\infty} dp v_p(x) v_p^*(x') \right]. \end{aligned}$$

The term inside the brackets corresponds to

$$\text{Closure relation} \quad \int_{-\infty}^{\infty} dp v_p(x) v_p^*(x') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{dp}{\hbar} e^{i\frac{p}{\hbar}(x-x')} \stackrel{(a)}{=} \delta(x - x'). \quad (1.20)$$

In (a) the following relation was used:

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{iku} = \delta(u).$$

Equation (1.20) is analogous to (1.15). In the same way, we can derive the orthonormalization relation using (a):

$$(v_p, v_{p'}) = \int_{-\infty}^{\infty} dx v_p^*(x) v_{p'}(x) = \frac{1}{2\pi} \int \frac{dx}{\hbar} e^{i\frac{x}{\hbar}(p'-p)} = \delta(p - p').$$

Therefore,

$$\text{Orthonormalization relation} \quad (v_p, v_{p'}) = \delta(p - p'). \quad (1.21)$$

Now instead of a kronecker delta, we have a delta function. If $p = p'$, the scalar product **diverges**: we see again that $v_p(x) \notin \mathcal{F}_x$. It is also said that $v_p(x)$ is "orthonormalized in the Dirac sense". The generalization to three dimension is given by

$$v_{\mathbf{p}}(\mathbf{r}) = \left(\frac{1}{2\pi\hbar} \right)^{3/2} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \quad (1.22)$$

The functions of $\{v_{\mathbf{p}}(\mathbf{r})\}$ basis now depend on the three continuous indices p_x, p_y, p_z condensed in \mathbf{p} . In addition,

$$\text{Expansion} \quad \psi(\mathbf{r}) = \int d^3p \bar{\psi}(\mathbf{p}) v_{\mathbf{p}}(\mathbf{r}) \quad (1.23)$$

$$\text{Coefficient expansion} \quad \bar{\psi}(\mathbf{p}) = (v_{\mathbf{p}}, \psi) = \int d^3r v_{\mathbf{p}}^*(\mathbf{r}) \psi(\mathbf{r}) \quad (1.24)$$

$$\text{Scalar product} \quad (\varphi, \psi) = \int d^3p \bar{\varphi}^*(\mathbf{p}) \bar{\psi}(\mathbf{p}) \quad (1.25)$$

$$\text{Closure relation} \quad \int d^3p v_{\mathbf{p}}(\mathbf{r}) v_{\mathbf{p}}^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (1.26)$$

$$\text{Orthonormalization relation} \quad (v_{\mathbf{p}}, v_{\mathbf{p'}}) = \delta(\mathbf{p} - \mathbf{p'}) \quad (1.27)$$

The $v_{\mathbf{p}}(\mathbf{r})$ can be considered to constitute a **continuous** basis.

Delta function

We can also consider a set of functions of \mathbf{r} , $\{\xi_{\mathbf{r}_0}(\mathbf{r})\}$, labeled by the continuous index $\mathbf{r}_0 = (x_0, y_0, z_0)$ and defined by

$$\xi_{\mathbf{r}_0}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_0). \quad (1.28)$$

Obviously, $\xi_{\mathbf{r}_0}(\mathbf{r})$ is not square-integrable: $\xi_{\mathbf{r}_0}(\mathbf{r}) \notin \mathcal{F}$.

Then, we can have the following

$$\text{Expansion} \quad \psi(\mathbf{r}) = \int d^3r_0 \psi(\mathbf{r}_0) \xi_{\mathbf{r}_0}(\mathbf{r}), \quad \text{and} \quad (1.29)$$

$$\text{Coefficient expansion} \quad \psi(\mathbf{r}_0) = (\xi_{\mathbf{r}_0}, \psi) = \int d^3r \xi_{\mathbf{r}_0}^*(\mathbf{r}) \psi(\mathbf{r}). \quad (1.30)$$

The equations are analogous to equations (1.11) and (1.12).

$\psi(\mathbf{r}_0)$ is the equivalent of c_i , which represent the components of the same function $\psi(\mathbf{r})$ in two different bases: $\{\xi_{\mathbf{r}_0}(\mathbf{r})\}$ and $\{u_i(\mathbf{r})\}$.

We also list, the other formulas:

$$\text{Scalar product} \quad (\varphi, \psi) = \int d^3r_0 \varphi^*(\mathbf{r}_0) \psi(\mathbf{r}_0) \quad (1.31)$$

$$\text{Closure relation} \quad \int d^3r_0 \xi_{\mathbf{r}_0}(\mathbf{r}) \xi_{\mathbf{r}_0}^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad (1.32)$$

$$\text{Orthonormalization relation} \quad (\xi_{\mathbf{r}_0}, \xi_{\mathbf{r}_0'}) = \delta(\mathbf{r}_0 - \mathbf{r}_0') \quad (1.33)$$

The $\xi_{\mathbf{r}_0}(\mathbf{r})$ can be considered to constitute a **continuous** basis.

A physical state must **always** correspond to a square-integrable wavefunction. In no case $v_p(\mathbf{r})$ and $\xi_{\mathbf{r}_0}(\mathbf{r})$ can represent the state of a particle. They are nothing more than intermediaries, useful for calculations.

Continuous orthonormal bases

We will denote a continuous orthonormal basis to a set of function of \mathbf{r} , $\{w_\alpha(\mathbf{r})\}$, labeled by a continuous index α , which satisfy the closure and orthonormalization relations:

$$\text{Orthonormalization relation} \quad (w_\alpha, w_{\alpha'}) = \int d^3r w_\alpha^*(\mathbf{r}) w_{\alpha'}(\mathbf{r}) = \delta(\alpha - \alpha') \quad (1.34)$$

$$\text{Closure relation} \quad \int d\alpha w_\alpha(\mathbf{r}) w_\alpha^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (1.35)$$

When $\alpha = \alpha'$, $(w_\alpha, w_{\alpha'})$ **diverges**. Therefore, $w_\alpha(\mathbf{r}) \notin \mathcal{F}$. Recall that this is a generalized continuous basis, so it can represent the plane waves and delta functions by setting $\alpha = \mathbf{p}$ and $\alpha = \mathbf{r}_0$, respectively.

In the case of mixed (discrete and continuous) basis $\{u_i(\mathbf{r}), w_\alpha(\mathbf{r})\}$, the orthonormalization relations are

$$\begin{aligned} \text{Orthonormalization relation for mixed basis} \quad & (u_i, u_j) = \delta_{ij} \\ & (w_\alpha, w_{\alpha'}) = \delta(\alpha - \alpha') \\ & (u_i, w_\alpha) = 0 \end{aligned} \quad (1.36)$$

And the closure relation becomes:

$$\text{Closure relation for mixed basis} \quad \sum_i u_i(\mathbf{r}) u_i^*(\mathbf{r}') + \int d\alpha w_\alpha(\mathbf{r}) w_\alpha^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (1.37)$$

We also list the expansion, coefficient of expansion and the scalar product for the continuous basis:

$$\text{Expansion} \quad \psi(\mathbf{r}) = \int d\alpha c(\alpha) w_\alpha(\mathbf{r}) \quad (1.38)$$

$$\text{Coefficient expansion} \quad c(\alpha) = (w_\alpha, \psi) = \int d^3r' w_\alpha^*(\mathbf{r}') \psi(\mathbf{r}') \quad (1.39)$$

$$\text{Scalar product} \quad (\varphi, \psi) = \int d\alpha b^*(\alpha) c(\alpha) \quad (1.40)$$

The squared norm of the wavefunction with itself is then

$$\text{Parseval's theorem} \quad (\psi, \psi) = \int d\alpha |c(\alpha)|^2. \quad (1.41)$$

Finally, all the formulas can thus be generalized from discrete basis of index i and continuous basis with index α (which can consider the plane wave and delta functions) through the following change of variables:

$$\text{Transformation } \{u_i(\mathbf{r})\} \longleftrightarrow \{w_\alpha(\mathbf{r})\} \quad \begin{array}{l} i \longleftrightarrow \alpha \\ \sum_i \longleftrightarrow \int d\alpha \\ \delta_{ij} \longleftrightarrow \delta(\alpha - \alpha') \end{array} \quad (1.42)$$

Table 1.1 Fundamental formulas for discrete and continuous basis.

| Property | Discrete basis $\{u_i(\mathbf{r})\}$ | Continuous basis $\{w_\alpha(\mathbf{r})\}$ |
|-----------------------------|--|--|
| Scalar product | $(\varphi, \psi) = \sum_i b_i^* c_i$ | $(\varphi, \psi) = \int d\alpha b^*(\alpha) c(\alpha)$ |
| Parseval | $(\psi, \psi) = \sum_i c_i ^2$ | $(\psi, \psi) = \int d\alpha c(\alpha) ^2$ |
| Orthonormalization relation | $(u_i, u_j) = \delta_{ij}$ | $(w_\alpha, w_{\alpha'}) = \delta(\alpha - \alpha')$ |
| Closure relation | $\sum_i u_i(\mathbf{r}) u_i^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ | $\int d\alpha w_\alpha(\mathbf{r}) w_\alpha^*(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ |
| Expansion | $\psi(\mathbf{r}) = \sum_i c_i u_i(\mathbf{r})$ | $\psi(\mathbf{r}) = \int d\alpha c(\alpha) w_\alpha(\mathbf{r})$ |
| Components | $c_i = (u_i, \psi)$ | $c(\alpha) = (w_\alpha, \psi)$ |

1.2 Dirac notation

Each quantum state of a particle will be characterized by a **state vector**, belonging to an abstract space \mathcal{E}_r , called the **state space** of the particle. The fact that the space \mathcal{F} is a subspace of L^2 means that \mathcal{E}_r is a subspace of a Hilbert space.

The introduction of these quantities permits a generalization of the formalism. In fact, there exist physical systems whose quantum description cannot be given by a wavefunction.

State vector

The quantum state of any physical system is characterized by a state vector, belonging to a space \mathcal{E} which is the state space of the system. The state space is the set of all of the possible states in which the system can exist.

1.2.1 Ket and Bra vectors

Ket vectors

Any element or vector of space \mathcal{E} is called a **key vector** or ket, and is represented by the symbol $|\cdot\rangle$. We shall define the space \mathcal{E}_r of the states of a particle by associating with every square-integrable function $\psi(r)$ a ket vector $|\psi\rangle$ of \mathcal{E}_r :

$$\psi(r) \in \mathcal{F} \implies |\psi\rangle \in \mathcal{E}_r. \quad (1.43)$$

Although \mathcal{F} and \mathcal{E}_r are **isomorphic**, we shall carefully distinguish between them. We see that the r -dependence no longer appears in $|\psi\rangle$: only appears ψ as an object that is used to extract information.

Dual space and bra vectors

A **linear function** χ is a linear operation which associates a complex number with every ket $|\psi\rangle$:

$$\begin{aligned} |\psi\rangle \in \mathcal{E} &\xrightarrow{\chi} \chi(|\psi\rangle) \in \mathbb{C} \\ \chi(\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle) &= \lambda_1\chi(|\psi_1\rangle) + \lambda_2\chi(|\psi_2\rangle). \end{aligned} \quad (1.44)$$

A linear functional is an operator that returns a complex number, while a linear operator returns another ket (vector).

The set of linear functionals defined on $|\psi\rangle \in \mathcal{E}$ constitutes a vector space, which is called **dual space** of \mathcal{E} and which will be symbolized by \mathcal{E}^* .

Any element, or vector of the space \mathcal{E}^* is called a **bra vector**, or bra and is denoted by $\langle\cdot|$.

The bra acts as a linear operator over the ket, which can be used to define the scalar product to return a complex number:

$$\text{Scalar product} \quad \langle\varphi|\psi\rangle = (|\varphi\rangle, |\psi\rangle). \quad (1.45)$$

We then have similar properties for the scalar product:

| | | |
|---|---|--|
| Adjoint | Linear to the second vector | Antilinear to the first vector |
| $\langle\varphi \psi\rangle = \langle\psi \varphi\rangle^*$ | $\langle\varphi \lambda_1\psi_1 + \lambda_2\psi_2\rangle = \lambda_1\langle\varphi \psi_1\rangle + \lambda_2\langle\varphi \psi_2\rangle$ | $\langle\lambda_1\varphi_1 + \lambda_2\varphi_2 \psi\rangle = \lambda_1^*\langle\varphi_1 \psi\rangle + \lambda_2^*\langle\varphi_2 \psi\rangle$ |

(1.46)

Relation bra-ket

There is an antilinear relation between a ket and its bra, so that we have the following multiplications by a scalar for the vectors

$$|\lambda\psi\rangle = \lambda|\psi\rangle \in \mathcal{E} \implies \langle\lambda\psi| = \lambda^*\langle\psi| \in \mathcal{E}^*, \quad \lambda \in \mathbb{C}. \quad (1.47)$$

Although to every ket there corresponds a bra, it is possible to find bras that have no corresponding kets such as delta functions and plane waves spaces. This dissymetry of the correspondence bra-ket is related to the existence of continuous basis for \mathcal{F}_x . This happens when the norm of the functions blow up making them not belong to \mathcal{F}_x , so we cannot associate a ket of \mathcal{E}_x with them. Nevertheless, their scalar product with a function of \mathcal{F}_x is defined, and this permits us to associate with them a linear function of \mathcal{E}_x : the bra

belonging to \mathcal{E}_x^* . However, we can define **generalized kets**, defined using functions that are not L^2 , but whose scalar product with every function of \mathcal{F}_x exists.

When working with plane waves and delta functions, we assume the following approximation:

$$|\xi_{x_0}\rangle \xrightarrow{\text{Refers to}} |\xi_{x_0}^{(\epsilon)}\rangle, \quad \text{and} \quad |v_{p_0}\rangle \xrightarrow{\text{Refers to}} |v_{p_0}^{(L)}\rangle, \quad (1.48)$$

where ϵ is very small and L very large compared to all other lengths of the problem, so we are always working in \mathcal{E}_x .

Note that

$$\begin{aligned} \xi_{x_0}^{(\epsilon)}(x) \in \mathcal{F}_x &\iff |\xi_{x_0}^{(\epsilon)}\rangle \in \mathcal{E}_x & v_{p_0}^{(L)}(x) \in \mathcal{F}_x &\iff |v_{p_0}^{(L)}\rangle \in \mathcal{E}_x \\ \lim_{\epsilon \rightarrow 0} |\xi_{x_0}^{(\epsilon)}\rangle &\notin \mathcal{E}_x & \lim_{L \rightarrow \infty} |v_{p_0}^{(L)}\rangle &\notin \mathcal{E}_x \\ \lim_{\epsilon \rightarrow 0} \langle \xi_{x_0}^{(\epsilon)} | &= \langle \xi_{x_0} | \in \mathcal{E}_x^* & \lim_{L \rightarrow \infty} \langle v_{p_0}^{(L)} | &= \langle v_{p_0} | \in \mathcal{E}_x^* \\ |\psi\rangle \in \mathcal{E}_x &\implies \langle \xi_{x_0} | \psi \rangle = \psi(x_0) & |\psi\rangle \in \mathcal{E}_x &\implies \langle v_{p_0} | \psi \rangle = \bar{\psi}(p_0) \end{aligned}, \quad \text{and} \quad (1.49)$$

In general, the dual space \mathcal{E}^* and the state space \mathcal{E} are not isomorphic, except that \mathcal{E} is finite-dimensional. Although to each ket there corresponds a bra, the converse is not true. In addition to use vector of \mathcal{E} (whose norm is finite), **generalized kets** with infinite norms but whose scalar product with every ket of \mathcal{E} is finite. Thus, to each bra of \mathcal{E}^* there will correspond a ket. But generalized kets do not represent physical states of the system.

1.2.2 Linear operators

A linear operator A associates with every ket $|\psi\rangle \in \mathcal{E}$ another ket $|\psi'\rangle \in \mathcal{E}$ linearly:

$$|\psi'\rangle = A|\psi\rangle \quad (1.50)$$

$$A(\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle) = \lambda_1 A|\psi_1\rangle + \lambda_2 A|\psi_2\rangle. \quad (1.51)$$

The product of two linear operators AB is defined by first acting B in the ket $|\psi\rangle$, and then A :

$$(AB)|\psi\rangle = A(B|\psi\rangle). \quad (1.52)$$

The commutator express the degree of difference between the change of order of operation:

$$[A, B] = AB - BA. \quad (1.53)$$

We call the **matrix element** of A between $|\varphi\rangle$ and $|\psi\rangle$, the scalar product that measure the collinearity between the action of the operator onto $|\varphi\rangle$:

$$\langle \varphi | A | \psi \rangle \in \mathbb{C}. \quad (1.54)$$

Projector

Lets assume that $\langle \psi | \psi \rangle = 1$ (normalized), we define the **projector** as an operator that projects a ket into another ket:

$$P_\psi = |\psi\rangle\langle\psi| \quad (1.55)$$

When it acts into a vector, it first compute the scalar product and then assign the value to the vector from which the product was computed:

$$P_\psi|\varphi\rangle = |\psi\rangle \underbrace{\langle\psi|\varphi\rangle}_{\text{number}}.$$

It is also *idempotent*, which means that

$$P_\psi^2 = P_\psi P_\psi = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = |\psi\rangle\langle\psi| = P_\psi. \quad (1.56)$$

The most generalized form is project a ket into a orthonormalized ($\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$) subspace $\{\varphi_q\} \in \mathcal{E}_q \subseteq \mathcal{E}$. Let P_q be then the linear operator

$$P_q = \sum_{i=1}^q |\varphi_i\rangle\langle\varphi_i|. \quad (1.57)$$

It then takes the ket, and compute the projection to every vector $|\varphi_i\rangle$ and then form a linear combination.

1.2.3 Hermitian conjugation (adjoint)

There is also possible to define actions of A on bras as $\langle\chi|A$, whose order is important.

We can also link with every linear operator A another linear operator A^\dagger , called the adjoint operator (or Hermitian conjugate) of A . The operator A associates with it another ket $|\psi'\rangle = A|\psi\rangle \in \mathcal{E}$. The correspondence between kets and bras permits us to define the action of operator A^\dagger on the bras:

$$|\psi\rangle \text{ corresponds to } \langle\psi| \implies |\psi'\rangle = A|\psi\rangle \text{ corresponds to } \langle\psi'| = \langle\psi|A^\dagger. \quad (1.58)$$

The relation $\langle\psi'| = \langle\psi|A^\dagger$ is **linear**, as

$$A(\lambda_1^*|\psi_1\rangle + \lambda_2^*|\psi_2\rangle) = \lambda_1^*A|\psi_1\rangle + \lambda_2^*A|\psi_2\rangle \text{ corresponds to } (\lambda_1\langle\psi_1| + \lambda_2\langle\psi_2|)A^\dagger = \lambda_1\langle\psi_1|A^\dagger + \lambda_2\langle\psi_2|A^\dagger.$$

Therefore, A^\dagger is a linear operator defined by

$$|\psi'\rangle = A|\psi\rangle \iff \langle\psi'| = \langle\psi|A^\dagger, \quad (1.59)$$

which also implies that

$$\langle\psi|A^\dagger|\varphi\rangle = \langle\varphi|A|\psi\rangle^*. \quad (1.60)$$

Properties

$$\begin{aligned} (A^\dagger)^\dagger &= A \\ (\lambda A)^\dagger &= \lambda^* A^\dagger \\ (A + B)^\dagger &= A^\dagger + B^\dagger \\ (AB)^\dagger &= B^\dagger A^\dagger \end{aligned}$$

Hermitian conjugation in Dirac notation

A ket $|\psi\rangle$ and its corresponding bra $\langle\psi|$ are said to be Hermitian conjugates of each other. In the same manner, A^\dagger is also called Hermitian conjugate operator of A .

The operation of Hermitian conjugate is followed by a very simple rule:

Rule of Hermitian conjugate

To obtain the adjoint of any expression composed of constants, kets, bras, and operators, one must:

| | |
|----------------------------------|---|
| Replace | $\left\{ \begin{array}{l} \text{the constants by their complex conjugates} \\ \text{the kets by the bras associated} \\ \text{the bras by the kets associated} \\ \text{the operators by their adjoints} \end{array} \right.$ |
| Reverse the order of the factors | Only constants can move around (commute) |

As an example,

$$(\lambda \langle u|A|v\rangle |w\rangle \langle \psi|)^{\dagger} = |\psi\rangle \langle w| \langle v|A^{\dagger}|u\rangle \underbrace{\lambda^*}_{\text{can move around}}$$

Hermitian operators

An operator A is said to be Hermitian if $A = A^{\dagger}$, which satisfy the following relations:

$$\langle \psi|A|\varphi\rangle = \langle \varphi|A|\psi\rangle^* \quad \text{and} \quad \langle A\varphi|\psi\rangle = \langle \varphi|A\psi\rangle.$$

In addition, the projector P_{ψ} is an Hermitian operator:

$$P_{\psi}^* = |\psi\rangle \langle \psi| = P_{\psi}. \quad (1.61)$$

The product of two Hermitian operators A, B is Hermitian only if $[A, B] = 0$.

1.3 Representations in state space

Choosing a representation means choosing an orthonormal (discrete or continuous) basis in the state space \mathcal{E} . Vectors and operators are then represented in this basis by *numbers*: components for the vectors, matrix elements for the operators.

We now translate all properties such as orthonormalization relation and closure relation to the Dirac notation.

1.3.1 Relations characteristic of an orthonormal basis

Orthonormalization relation

A set of kets, discrete $\{|u_i\rangle\}$ or continuous $\{|w_{\alpha}\rangle\}$ is said to be orthonormal if they satisfy the following equation:

$$\text{Orthonormalization relation} \quad \begin{array}{l} \langle u_i|u_j\rangle = \delta_{ij} \\ \langle w_{\alpha}|w_{\alpha'}\rangle = \delta(\alpha - \alpha') \end{array}. \quad (1.62)$$

As can be seen, for a continuous set $\langle w_{\alpha}|w_{\alpha}\rangle$ **does not exist**: the $|w_{\alpha}\rangle$ have an infinite norm and therefore do not belong to \mathcal{E} . Nevertheless, the vectors of \mathcal{E} can be expanded on the $|w_{\alpha}\rangle$. It is useful then to accept $|w_{\alpha}\rangle$ as *generalized kets*.

Closure relation

A discrete or continuous set constitutes a basis if every ket $|\psi\rangle \in \mathcal{E}$ has a **unique** expansion on $|u_i\rangle$ or $|w_\alpha\rangle$:

$$\begin{aligned} \text{Closure relation} \quad & \begin{aligned} |\psi\rangle &= \sum_i c_i |u_i\rangle \\ |\psi\rangle &= \int d\alpha c(\alpha) |w_\alpha\rangle \end{aligned}, \end{aligned} \quad (1.63)$$

whose components are obtained multiplying $\langle u_j|$ ($\langle w_{\alpha'}|$) in the closure relation and using equation (1.62):

$$\begin{aligned} \text{Coefficient expansion} \quad & \begin{aligned} \langle u_j|\psi\rangle &= c_j \\ \langle w_{\alpha'}|\psi\rangle &= c(\alpha') \end{aligned}. \end{aligned} \quad (1.64)$$

We can reexpress the expansion employing the coefficient expansion equations:

$$\begin{aligned} |\psi\rangle &= \sum_i c_i |u_i\rangle = \sum_i \langle u_i|\psi\rangle |u_i\rangle = \sum_i |u_i\rangle \langle u_i|\psi\rangle = \left[\sum_i |u_i\rangle \langle u_i| \right] |\psi\rangle = P_{\{u_i\}} |\psi\rangle, \\ |\psi\rangle &= \int d\alpha c(\alpha) |w_\alpha\rangle = \int d\alpha \langle w_\alpha|\psi\rangle |w_\alpha\rangle = \int d\alpha |w_\alpha\rangle \langle w_\alpha|\psi\rangle = \left[\int d\alpha |w_\alpha\rangle \langle w_\alpha| \right] |\psi\rangle = P_{\{w_\alpha\}} |\psi\rangle. \end{aligned}$$

We then have the projector onto a discrete and continuous basis:

$$\begin{aligned} \text{Projectors} \quad & \begin{aligned} P_{\{u_i\}} &= \sum_i |u_i\rangle \langle u_i| = \mathbb{1} \\ P_{\{w_\alpha\}} &= \int d\alpha |w_\alpha\rangle \langle w_\alpha| = \mathbb{1} \end{aligned} \end{aligned} \quad \begin{aligned} & \text{Closure relation,} \\ & (1.65) \end{aligned}$$

where $\mathbb{1}$ denotes the identity operator in \mathcal{E} . These relations express the fact that $\{|u_i\rangle\}$ and $\{|w_\alpha\rangle\}$ constitute bases.

Table 1.2 Fundamental formulas for calculation in the $\{|u_i\rangle\}$ and $\{|w_\alpha\rangle\}$ representations.

| $\{ u_i\rangle\}$ representation | $\{ w_\alpha\rangle\}$ representation |
|--|---|
| $\langle u_i u_j\rangle = \delta_{ij}$ | $\langle w_\alpha w_{\alpha'}\rangle = \delta(\alpha - \alpha')$ |
| $P_{\{u_i\}} = \sum_i u_i\rangle \langle u_i = \mathbb{1}$ | $P_{\{w_\alpha\}} = \int d\alpha w_\alpha\rangle \langle w_\alpha = \mathbb{1}$ |

1.3.2 Representation of kets and bras

In the $\{|u_i\rangle\}$ basis, the ket $|\psi\rangle$ is represented by a set of its components $x_i \langle u_i|\psi\rangle$. These numbers are arranged vertically to form a column matrix. On the other hand, for continuous basis $\{|w_\alpha\rangle\}$, the ket $|\psi\rangle$ is represented by a continuous **infinity** of numbers $c(\alpha) = \langle w_\alpha|\psi\rangle$: a function of α . We then draw a vertical axis with the values of $c(\alpha)$:

$$\begin{aligned} |\psi\rangle_{\{|u_i\rangle\}} &= \mathbb{1}|\psi\rangle = P_{\{u_i\}}|\psi\rangle = \sum_i |u_i\rangle \langle u_i|\psi\rangle = \sum_i c_i |u_i\rangle, \\ |\psi\rangle_{\{|w_\alpha\rangle\}} &= \mathbb{1}|\psi\rangle = P_{\{w_\alpha\}}|\psi\rangle = \int d\alpha |w_\alpha\rangle \langle w_\alpha|\psi\rangle = \int d\alpha c(\alpha) |w_\alpha\rangle. \end{aligned}$$

Then,

$$|\psi\rangle_{\{|u_i\rangle\}} = \begin{bmatrix} \langle u_1|\psi\rangle \\ \langle u_2|\psi\rangle \\ \vdots \\ \langle u_i|\psi\rangle \\ \vdots \end{bmatrix}, \quad \text{and} \quad |\psi\rangle_{\{|w_\alpha\rangle\}} = \alpha \downarrow \begin{bmatrix} \vdots \\ \vdots \\ \langle w_\alpha|\psi\rangle \\ \vdots \\ \vdots \end{bmatrix}. \quad (1.66)$$

Something similar happens to the respective bras:

$$\begin{aligned} \langle\varphi|_{\{|u_i\rangle\}} &= \langle\varphi|\mathbb{1} = \langle\varphi|P_{\{|u_i\rangle\}} = \sum_i \langle\varphi|u_i\rangle \langle u_i| = \sum_i b_i^* \langle u_i|, \\ \langle\varphi|_{\{|w_\alpha\rangle\}} &= \langle\varphi|\mathbb{1} = \langle\varphi|P_{\{|w_\alpha\rangle\}} = \int d\alpha \langle\varphi|w_\alpha\rangle \langle w_\alpha| = \int d\alpha b^*(\alpha) \langle\varphi|. \end{aligned}$$

We can see that the components of the bra are the complex conjugates of the components $b_i = \langle u_i|\varphi\rangle$ and $b(\alpha) = \langle w_\alpha|\varphi\rangle$ of the ket $|\varphi\rangle$ associated with $\langle\varphi|$.

Let us then arrange them horizontally, to form a row matrix:

$$\langle\varphi|_{\{|u_i\rangle\}} = [\langle\varphi|u_1\rangle \quad \langle\varphi|u_2\rangle \quad \cdots \quad \langle\varphi|u_i\rangle \quad \cdots], \quad \text{and} \quad (1.67)$$

$$\langle\varphi|_{\{|w_\alpha\rangle\}} = \begin{matrix} \alpha \\ \rightarrow \\ [\cdots \quad \cdots \quad \langle\varphi|w_\alpha\rangle \quad \cdots \quad \cdots] \end{matrix}. \quad (1.68)$$

The scalar product is then given by a **matrix multiplication**:

$$\langle\varphi|\psi\rangle = \langle\varphi|\mathbb{1}|\psi\rangle = \langle\varphi|P_{\{|u_i\rangle\}}|\psi\rangle = \sum_i \langle\varphi|u_i\rangle \langle u_i|\psi\rangle = \sum_i b_i^* c_i \quad (1.69)$$

$$\langle\varphi|\psi\rangle = \langle\varphi|\mathbb{1}|\psi\rangle = \langle\varphi|P_{\{|w_\alpha\rangle\}}|\psi\rangle = \int d\alpha \langle\varphi|w_\alpha\rangle \langle w_\alpha|\psi\rangle = \int d\alpha b^*(\alpha) c(\alpha). \quad (1.70)$$

1.3.3 Representation of operators

Representation of A by a square matrix

Given a linear operator A , we can in $\{|u_i\rangle\}$ or $\{|w_\alpha\rangle\}$ basis, associate with it a series of numbers defined by

$$A_{ij} = \langle u_i|A|u_j\rangle, \quad \text{or} \quad A(\alpha, \alpha') = \langle w_\alpha|A|w_{\alpha'}\rangle. \quad (1.71)$$

They are arranged into a square matrix, as

$$\begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1j} & \cdots \\ A_{21} & A_{22} & \cdots & A_{2j} & \cdots \\ \vdots & \vdots & & \vdots & \\ A_{i1} & A_{i2} & \cdots & A_{ij} & \cdots \\ \vdots & \vdots & & \vdots & \end{bmatrix}, \quad \text{or} \quad \alpha \downarrow \begin{matrix} \alpha' \\ \rightarrow \\ \begin{bmatrix} \vdots \\ \vdots \\ A(\alpha, \alpha') & \cdots \\ \vdots \end{bmatrix} \end{matrix}. \quad (1.72)$$

For the case of the matrix representing the operator AB in the $\{|u_i\rangle\}$ basis, we have:

$$\langle u_i|AB|u_j\rangle = \langle u_i|A\mathbb{1}|u_j\rangle = \langle u_i|AP_{\{u_k\}}B|u_j\rangle = \sum_k \langle u_i|A|u_k\rangle \langle u_k|B|u_j\rangle = \sum_k A_{ik}B_{kj}.$$

Representation of the ket $|\psi'\rangle = A|\psi\rangle$

Knowing the components of $|\psi\rangle$ and the matrix elements of A in a given representation, how can we calculate the components of $|\psi'\rangle = S|\psi\rangle$ in the same representation?

We know that in the $\{|u_i\rangle\}$ and $\{|w_\alpha\rangle\}$ basis, we have

$$c'_i = \langle u_i|\psi'\rangle = \langle u_i|A|\psi\rangle, \quad \text{and} \quad c'(\alpha) = \langle w_\alpha|\psi'\rangle.$$

Inserting the closure relation between A and $|\psi\rangle$:

$$\begin{aligned} c'_i &= \langle u_i|A\mathbb{1}|\psi\rangle = \langle u_i|AP_{\{u_j\}}|\psi\rangle = \sum_j \langle u_i|A|u_j\rangle \langle u_j|\psi\rangle = \sum_j A_{ij}c_j \\ c'(\alpha) &= \langle w_\alpha|A\mathbb{1}|\psi\rangle = \int d\alpha' \langle w_\alpha|A|w_{\alpha'}\rangle \langle w_{\alpha'}|\psi\rangle = \int d\alpha' A(\alpha, \alpha')c(\alpha'). \end{aligned}$$

We see that the column matrix representing $|\psi'\rangle$ is equal to the matrix multiplication of the column matrix $|\psi\rangle$ and the square matrix A .

Expression for the number $\langle\varphi|A|\psi\rangle$

On the other hand, we can derive an expression for $\langle\varphi|A|\psi\rangle$ for both basis:

$$\begin{aligned} \langle\varphi|A|\psi\rangle &= \langle\varphi|P_{\{u_i\}}AP_{\{u_j\}}|\psi\rangle = \sum_{i,j} \langle\varphi|u_i\rangle \langle u_i|A|u_j\rangle \langle u_j|\psi\rangle = \sum_{i,j} b_i^* A_{ij}c_j, \\ \langle\varphi|P_{\{w_\alpha\}}AP_{\{w_{\alpha'}\}}|\psi\rangle &= \iint d\alpha d\alpha' \langle\varphi|w_\alpha\rangle \langle w_\alpha|A|w_{\alpha'}\rangle \langle w_{\alpha'}|\psi\rangle = \iint d\alpha d\alpha' b^*(\alpha) A(\alpha, \alpha')c(\alpha'). \end{aligned}$$

Thus, the term $\langle\varphi|A|\psi\rangle$ which is a number, can be computed as a matrix multiplication of the column vector $|\psi\rangle$ by the matrix A , and then by the row vector $\langle\varphi|$.

Matrix representation of A^\dagger

The adjoint of A can also be written as:

$$\begin{aligned} (A^\dagger)_{ij} &= \langle u_i|A^\dagger|u_j\rangle = \langle u_j|A|u_i\rangle^* = A_{ji}^* \\ A^\dagger(\alpha, \alpha') &= \langle w_\alpha|A^\dagger|w_{\alpha'}\rangle = \langle w_{\alpha'}|A|w_\alpha\rangle^* = A^*(\alpha', \alpha). \end{aligned} \tag{1.73}$$

The matrices representing A and A^\dagger are then Hermitian conjugates of each other.

If A is Hermitian, then $A_{ij} = A_{ji}^*$ and $A(\alpha, \alpha') = A^*(\alpha', \alpha)$. A hermitian operator is therefore represented by a Hermitian matrix. For $i = j$, $\alpha = \alpha'$ we see that $A_{ii} = A_{ii}^*$, $A(\alpha, \alpha) = A^*(\alpha, \alpha)$. Thus,

The diagonal elements of a Hermitian matrix are therefore always real numbers.

1.3.4 Change of representation

We can representate a ket $|\psi\rangle$ in different bases, similar to representing a point in space by cartesian and spherical coordinates. The relation of these two representation allow us to turn from one to the other easily.

If we assume an old discrete basis $\{|u_i\rangle\}$ to a new one $\{|t_k\rangle\}$, the change of basis is defined by specifying the components $S_{ik} = \langle u_i | t_k \rangle$ of each kets of the new basis in terms of the kets of the old one. The adjoint is: $(S^\dagger)_{ki} = (S_{ik})^* = \langle t_k | u_i \rangle$. This transformation matrix is **unitary**: $S^\dagger S = S S^\dagger = I$.

We will derive the transformation for a ket, a bra, and the matrix elements of an operator using the closure relation of each basis as explained in the derivation.

$$\begin{aligned}
\langle t_k | \psi \rangle &= \langle t_k | \mathbb{1} | \psi \rangle = \langle t_k | P_{\{u_i\}} | \psi \rangle = \sum_i \langle t_k | u_i \rangle \langle u_i | \psi \rangle = \sum_i S_{ki}^\dagger \langle u_i | \psi \rangle \\
\langle u_i | \psi \rangle &= \langle u_i | \mathbb{1} | \psi \rangle = \langle u_i | P_{\{t_k\}} | \psi \rangle = \sum_k \langle u_i | t_k \rangle \langle t_k | \psi \rangle = \sum_k S_{ik} \langle t_k | \psi \rangle \\
\langle \psi | t_k \rangle &= \langle \psi | \mathbb{1} | t_k \rangle = \langle \psi | P_{\{u_i\}} | t_k \rangle = \sum_i \langle \psi | u_i \rangle \langle u_i | t_k \rangle = \sum_i \langle \psi | u_i \rangle S_{ik} \\
\langle \psi | u_i \rangle &= \langle \psi | \mathbb{1} | u_i \rangle = \langle \psi | P_{\{t_k\}} | u_i \rangle = \sum_k \langle \psi | t_k \rangle \langle t_k | u_i \rangle = \sum_k \langle \psi | t_k \rangle S_{ki}^\dagger \\
A_{kl} &= \langle t_k | A | t_l \rangle = \langle t_k | \mathbb{1} A \mathbb{1} | t_l \rangle = \langle t_k | P_{\{u_i\}} A P_{\{u_j\}} | t_l \rangle = \sum_{i,j} \langle t_k | u_i \rangle \langle u_i | A | u_j \rangle \langle u_j | t_l \rangle = \sum_{i,j} S_{ki}^\dagger A_{ij} S_{jl} \\
A_{ij} &= \langle u_i | A | u_j \rangle = \langle u_i | \mathbb{1} A \mathbb{1} | u_j \rangle = \langle u_i | P_{\{t_k\}} A P_{\{t_l\}} | u_j \rangle = \sum_{k,l} \langle u_i | t_k \rangle \langle t_k | A | t_l \rangle \langle t_l | u_j \rangle = \sum_{k,l} S_{ik} A_{kl} S_{lj}^\dagger.
\end{aligned}$$

The final results are shown in table

Table 1.3 Transformation of a ket, bra, and matrix elements from one basis to another.

| Transformation | Expression |
|--|---|
| Ket components $\{u_i\} \longrightarrow \{t_k\}$ representation | $\langle t_k \psi \rangle = \sum_i S_{ki}^\dagger \langle u_i \psi \rangle$ |
| Ket components $\{t_k\} \longrightarrow \{u_i\}$ representation | $\langle u_i \psi \rangle = \sum_k S_{ik} \langle t_k \psi \rangle$ |
| Bra components $\{u_i\} \longrightarrow \{t_k\}$ representation | $\langle \psi t_k \rangle = \sum_i \langle \psi u_i \rangle S_{ik}$ |
| Bra components $\{t_k\} \longrightarrow \{u_i\}$ representation | $\langle \psi u_i \rangle = \sum_k \langle \psi t_k \rangle S_{ki}^\dagger$ |
| Matrix elements $\{u_{i,j}\} \longrightarrow \{t_{k,l}\}$ representation | $A_{kl} = \sum_{i,j} S_{ki}^\dagger A_{ij} S_{jl}$ |
| Matrix elements $\{t_{k,l}\} \longrightarrow \{u_{i,j}\}$ representation | $A_{ij} = \sum_{k,l} S_{ik} A_{kl} S_{lj}^\dagger$ |

1.4 Eigenvalue equations. Observables

1.4.1 Eigenket and eigenbra equations

$|\psi\rangle$ is said to be an **eigenvector** (or eigenket) of the linear operator A if

$$\text{Eigenket equation of } A \quad A|\psi\rangle = \lambda|\psi\rangle, \quad \lambda \in \mathbb{C}. \quad (1.74)$$

This eigenket equation possesses solutions only when λ takes on certain values, called **eigenvalues** of A . The set of the eigenvalues is called **spectrum** of A .

Collinear of an eigenvector is also an eigenvector

If $|\psi\rangle$ is an eigenvector of A with eigenvalue λ , then $\alpha|\psi\rangle$, $\alpha \in \mathbb{C}$ is also an eigenvector of A .

The eigenvalue λ is called *non-degenerate* (or simple) when its corresponding eigenvector is **unique** to within a constant factor (collinear). On the other hand, if there exists at least two linearly independent eigenkets with the **same** eigenvalue, the eigenvalue is said to be *degenerate*. Its *degree of degeneracy* g is then the number of linearly independent eigenvectors $|\psi^i\rangle$, $i = \{1, 2, \dots, g\}$ associated with it.

The set of eigenkets associated with a degenerate eigenvalue constitutes a g -dimensional vector space called **eigensubspace** of λ .

Taking the adjoint of the eigenket equation yields its corresponding form to eigenbra equation

$$\text{Eigenbra equation of } A^\dagger \quad \langle\psi|A^\dagger = \lambda^*\langle\psi|. \quad (1.75)$$

If $|\psi\rangle$ is an eigenket of A with λ , it can also be said that $\langle\psi|$ is an eigenbra of A^\dagger with λ^* .

Finding the eigenvalues and eigenvector in an operator

Assuming the state space is of finite dimension N , granting the generalization to an infinite-dimensional state space.

Choosing $\{|u_i\rangle\}$, lets us project the vector (1.74) onto the various orthonormal basis vectors $|u_i\rangle$:

$$\langle u_i|A|\psi\rangle = \lambda\langle u_i|\psi\rangle. \quad (1.76)$$

Inserting the closure relation between A and $|\psi\rangle$:

$$\langle u_i|A\mathbb{1}|\psi\rangle = \sum_j \underbrace{\langle u_i|A|u_j\rangle}_{A_{ij}} \underbrace{\langle u_j|\psi\rangle}_{c_j} = \lambda \underbrace{\langle u_i|\psi\rangle}_{c_i} \longrightarrow \sum_j [A_{ij} - \lambda\delta_{ij}]c_j = 0. \quad (1.77)$$

Equation (1.77) is a system of equations with N equations and N unknowns c_j . It has non-trivial solution iff its characteristic equation is zero:

$$\text{Characteristic equation of the eigenket equation} \quad P(\lambda) = \det[A - \lambda I] = 0. \quad (1.78)$$

This expression enable us to determine the spectrum of A . The characteristic equation is **independent** of the representation chosen. Then,

The eigenvalues of an operator are the roots λ of its N th order characteristic equation $P(\lambda)$.

Determination of eigenvectors

Given a transformation $T(v) = Mv : V \in \mathbb{C}^N \longrightarrow W \in \mathbb{C}^N$, the theorem says:

$$\dim(V) = \text{rank}(T) + \text{null}(T), \quad (1.79)$$

where

$\dim(V)$ = Number of columns of V

$\text{rank}(T)$ = Number of independent equations (non zero rows)

$\text{null}(T) = \dim[\ker(T)]$ = Number of free variables, degree of freedom (dof).

In our case, $T(v) = Mv = (A - \lambda I)v$ and $\dim(V) = N$.

Based on the nature of the eigenvalue, we can have different eigenvalues but also repeated. Therefore, we define the following useful quantities:

- **Algebraic multiplicity (AM)** Number of repetition of the eigenvalue (degree of degeneracy g).
- **Geometric multiplicity (GM)** Dimension of the subspace that the eigenvalues generate (how many linearly independent eigenvectors exist for that eigenvalue).

We then can have the following three cases:

- $AM = GM = 1$ Only one eigenvector corresponds to the eigenvalue (within a constant factor). At the moment of substituting an eigenvalue λ_0 into equation (1.77) there will be $\text{rank}(M) = N - 1$ independent equations so one equation is redundant. When this happens, $\text{null}(M) = 1$ free variable (or degree of freedom, dof) c_1 is available which can be defined arbitrarily and from which all other variables can be expressed.

If we fix c_1 , then all c_j are proportional to it:

$$c_j = \alpha_j^0 c_1 \quad (\alpha_1^0 = 1). \quad (1.80)$$

the $N - 1$ coefficients α_j^0 , $j \neq 1$ are determined from the matrix elements A_{ij} and λ_0 . The eigenvectors associated with λ_0 differ only by the value chosen for c_1 . They are therefore all given by

$$|\psi_0(c_1)\rangle = \sum_j \alpha_j^0 c_1 |u_j\rangle = c_1 |\psi_0\rangle, \quad \text{with} \quad |\psi_0\rangle = \sum_j \alpha_j^0 |u_j\rangle. \quad (1.81)$$

When λ_0 is simple, only one eigenvector corresponds to it.

Ejemplo 1.1

In the matrix

$$A = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 2 & 1 \\ 0 & 0 & 3 \end{bmatrix}$$

Simple eigenvalues

the eigenvalues are $\lambda \in \{1, 2, 3\}$. Lets make $\lambda_0 = 1$ and replace it into the eigenvalue problem:

$$(A - \lambda I)v = (A - I)v = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 1 & 1 \\ 0 & 0 & 2 \end{bmatrix} v = 0$$

We see that there is no value in the first column, meaning that x_1 is free whereas $x_2 = x_3 = 0$. Therefore, the eigenvector is $v_1 = (1 \ 0 \ 0)$.

- $AM = GM > 1$ When evaluating λ_0 , the system will have $\text{rank}(M) = N - p$ independent equations ($1 < p < q$). To the eigenvalue λ_0 there corresponds an eigensubspace of dimension $\text{null}(M) = p$, and λ_0 is a p -fold degenerate eigenvalue.

Assuming that for $\lambda = \lambda_0$ is composed of $N - 2$ linearly independent equations. These equations enable us to calculate the coefficients c_j in terms of any of them, for example c_1 and c_2 :

$$c_j = \beta_j^0 c_1 + \gamma_j^0 c_2.$$

All the eigenvectors associated with λ_0 are then of the form

$$|\psi_0(c_1, c_2)\rangle = c_1|\psi_0^1\rangle + c_2|\psi_0^2\rangle, \quad \text{with} \quad |\psi_0^1\rangle = \sum_j \beta_j^0 |u_j\rangle, \quad |\psi_0^2\rangle = \sum_j \gamma_j^0 |u_j\rangle. \quad (1.82)$$

The vectors $|\psi_0(c_1, c_2)\rangle$ do indeed constitute a two-dimensional vector space, this being characteristic of a two-fold degenerate eigenvalue.

- $AM > GM > 1$ In this case, the subspace is less than the degree of degeneracy and therefore not all degenerate eigenvectors are linearly independent. This means that there is not enough information to create a basis. However, techniques such as Jordan canonical form helps to create generalized eigenvector and to span the whole space.

When an operator is Hermitian, it can be shown that the degree of degeneracy p of an eigenvalue λ is always equal to the multiplicity of the corresponding root in the characteristic equations. In a space of finite dimension N , a Hermitian operator always has N linearly independent eigenvectors: this operator can therefore be diagonalized.

1.4.2 Observables

Properties of the eigenvalues and eigenvectors of a Hermitian operator

- The eigenvalues of a Hermitian operator are real.
- Two eigenvectors of a Hermitian operator corresponding to two different eigenvalues are orthogonal.

Definition of a observable

Consider a Hermitian operator A with discrete spectrum. The degree of degeneracy of the eigenvalue a_n is denoted by g_n . We shall denote by $|\psi_n^i\rangle$ g_n linearly independent vectors chosen in the eigensubspace \mathcal{E}_n of a_n :

$$A|\psi_n^i\rangle = a_n|\psi_n^i\rangle, \quad i = 1, 2, \dots, g_n. \quad (1.83)$$

Every vector of \mathcal{E}_n is orthogonal to every vector of another subspace $\mathcal{E}_{n'}$: $\langle \psi_n^i | \psi_{n'}^j \rangle = 0$, $n \neq n'$.

Inside the subspace \mathcal{E}_n , the $|\psi_n^i\rangle$ can always be chosen orthonormal, such that

$$\langle \psi_n^i | \psi_n^j \rangle = \delta_{ij}. \quad (1.84)$$

If such a choice is made, the result is an orthonormal system of eigenvectors of A : the $|\psi_n^i\rangle$ satisfying the relations:

$$\langle \psi_n^i | \psi_{n'}^{i'} \rangle = \delta_{nn'} \delta_{ii'}. \quad (1.85)$$

Observable

The Hermitian operator A is an **observable** if its eigenvectors **form a basis** in the state space:

$$\text{Closure relation of an observable} \quad \sum_{n=1}^{\infty} \sum_{i=1}^{g_n} |\psi_n^i\rangle \langle \psi_n^i| = \mathbb{1}. \quad (1.86)$$

The projector onto the subspace \mathcal{E}_n is written as:

$$P_n = \sum_{i=1}^{g_n} |\psi_n^i\rangle \langle \psi_n^i|. \quad (1.87)$$

The observable A is the given by:

$$A = \sum_n a_n P_n. \quad (1.88)$$

Equation (1.86) can be generalized to include cases of continuous spectrum using the previous table of the first section.

If A has a mixed spectrum, then it is an observable if this system form a basis, that is, if

$$\sum_n \sum_{i=1}^{g_n} |\psi_n^i\rangle \langle \psi_n^i| + \int_{\nu_1}^{\nu_2} d\nu |\psi_\nu\rangle \langle \psi_\nu| = \mathbb{1}. \quad (1.89)$$

The projector P_ψ is an observable

The projector $P_\psi = |\psi\rangle \langle \psi|$ is an observable. We know that it is Hermitian, and that its eigenvalues are 1 and 0, the first one is simple and the other infinitely degenerate. It can be shown that any ket $|\psi\rangle$ can be expanded on these eigenkets, therefore P_ψ is an observable.

1.4.3 Sets of commuting observables

Important theorems

Theorem I

If two operators A and B commute, and if $|\psi\rangle$ is an eigenvector of A , $B|\psi\rangle$ is also an eigenvector of A , with the same eigenvalue.

Another form:

If two operators A and B commute, every eigensubspace of A is globally invariant under the action of B ($B|\psi\rangle$ belongs to the eigensubspace \mathcal{E}_a of A , corresponding to the eigenvalue a).

Theorem II (consequence of theorem I)

If two observables A and B commute, and if $|\psi_1\rangle$ and $|\psi_2\rangle$ are two eigenvectors of A with different eigenvalues, the matrix element $\langle\psi_1|B|\psi_2\rangle$ is zero.

Theorem III

If two observables A and B commute, one can construct an orthonormal basis of the state space with eigenvectors common to A and B .

Let's prove the theorem III. Consider two commuting observables A and B , with discrete spectrum. Since A is observable, there exists at least one orthonormal system of eigenvectors $|u_n^i\rangle$ which forms a basis in the state space:

$$A|u_n^i\rangle = a_n|u_n^i\rangle, \quad \begin{matrix} n = 1, 2, \dots \\ i = 1, 2, \dots, g_n \end{matrix} \quad (1.90)$$

We also have $\langle u_n^i | u_{n'}^{i'} \rangle = \delta_{nn'} \delta_{ii'}$. What does the matrix look like which represents B in the $\{|u_n^i\rangle\}$ basis? We know that the matrix elements $\langle u_n^i | B | u_{n'}^{i'} \rangle$ are zero when $n \neq n'$ (theorem II). Let us arrange the basis vectors $|u_n^i\rangle$ in the order:

$$|u_1^1\rangle, |u_1^2\rangle, \dots, |u_1^{g_1}\rangle; |u_2^1\rangle, \dots, |u_2^{g_2}\rangle; |u_3^1\rangle, \dots$$

We then obtain for B a block-diagonal matrix of the form:

$$\begin{bmatrix} & \mathcal{E}_1 & & \mathcal{E}_2 & & \mathcal{E}_3 & \dots \\ \mathcal{E}_1 & \begin{matrix} \ddots & & \ddots \\ & \ddots & \ddots \end{matrix} & & 0 & & 0 & 0 \\ & & & & & & \\ \mathcal{E}_2 & & & \begin{matrix} \ddots & \ddots & \ddots \\ & \ddots & \ddots \\ \ddots & \ddots & \ddots \end{matrix} & & 0 & 0 \\ & & & & & & \\ \mathcal{E}_3 & 0 & & 0 & & \ddots & 0 \\ \vdots & 0 & & 0 & & 0 & \ddots & \ddots \\ & & & & & & \ddots & \ddots \end{bmatrix} \quad (1.91)$$

Then the degeneracy of the eigenvalue is 1, then the block reduces to a 1×1 matrix. In the column associated with $|u_n\rangle$ all the other matrix elements are zero, this expresses the fact that $|u_n\rangle$ is an eigenvector common to A and B . When a_n is a g_n -degenerate eigenvalue of A , the block which represents B in \mathcal{E}_n is not, in general, diagonal: the $|u_n^i\rangle$ are not, in general, eigenvectors of B . The action of A in the g_n eigenvectors $|u_n^i\rangle$ reduces to $a_n|u_n^i\rangle$, the matrix representing the restriction of A to within \mathcal{E}_n is equal to $a_n I_{g_n \times g_n}$. The matrix representing the operator A in \mathcal{E}_n is always diagonal and equal to $a_n I_{g_n \times g_n}$.

We use this property to obtain a basis of \mathcal{E}_n composed of vectors that are also eigenvectors of B . The matrix representing B in \mathcal{E}_n when the basis is chosen is

$$\{|u_n^i\rangle, \quad i = 1, 2, \dots, g_n\}, \quad (1.92)$$

has for its elements:

$$\beta_{ij}^{(n)} = \langle u_n^i | B | u_n^j \rangle. \quad (1.93)$$

This matrix is Hermitian, since B is a Hermitian operator. It is therefore diagonalizable: one can find a new basis $\{|v_n^i\rangle; i = 1, 2, \dots, g_n\}$ in which B is represented by a diagonal matrix:

$$\langle v_n^i | B | v_n^j \rangle = \beta_i^n \delta_{ij}. \quad (1.94)$$

This means that the new basis vectors in \mathcal{E}_n are eigenvectors of B :

$$B | v_n^i \rangle = \beta_i^{(n)} | v_n^i \rangle. \quad (1.95)$$

These vectors are automatically eigenvectors of A with an eigenvalue a_n since they belong to \mathcal{E}_n .

Eigenvectors of A associated with degenerate eigenvalues are not necessarily eigenvectors of B . It is always possible to choose, in every eigensubspace of A , a basis of eigenvectors common to A and B .

If we perform this operation in all the subspaces \mathcal{E}_n , we obtain a basis of \mathcal{E} , formed by eigenvectors common to A and B .

We shall denote by $|u_{n,p}^i\rangle$ the eigenvectors common to A and B :

$$A | u_{n,p}^i \rangle = a_n | u_{n,p}^i \rangle, \quad \text{and} \quad B | u_{n,p}^i \rangle = b_p | u_{n,p}^i \rangle. \quad (1.96)$$

The index i will be used to distinguish between different basis vectors which correspond to the same eigenvalues a_n and b_p .

Complete sets of commuting observables (C.S.C.O.)

Consider an observable A and a basis \mathcal{E} composed of eigenvectors $|u_n^i\rangle$ of A .

If none of the eigenvalues of A is degenerate, the various basis vectors of \mathcal{E} can be labelled by the eigenvalue a_n (index i is not necessary). Therefore, specifying the eigenvalue determines in a unique way the corresponding eigenvector. In other words, there exists only one basis of \mathcal{E} formed by the eigenvectors of A . It is said that the observable A constitutes, by itself, a C.S.C.O.

On the other hand, if at least one eigenvalue of A is degenerate, specifying a_n is no longer always sufficient to characterize a basis vector: the basis of eigenvectors of A is not unique. One can choose any basis inside each of the degenerate eigensubspaces \mathcal{E}_n . We can choose another observable B which commutes with A to construct an orthonormal basis of eigenvectors common to A and B . A and B form a C.S.C.O. if this basis is unique, that is, if to each of the possible pairs of eigenvalues $\{a_n, b_p\}$ there corresponds only one basis vector. For A and B to constitute a C.S.C.O., it is necessary and sufficient that, inside each of these subspaces, all the g_n eigenvalues of B be distinct. We can add indefinitely observables until we reach the C.S.C.O.

A set of observables A, B, C, \dots is called a complete set of commuting observables if:

- (i) all the observables commute by pairs.
- (ii) specifying the eigenvalue of all the operators determines a unique common eigenvector. The ket then is denoted as $|a_n, b_p, c_r, \dots\rangle$.

This means that they are C.S.C.O. if there exists a unique orthonormal basis of common eigenvectors.

Identification of CSCOs is necessary in order to construct physically meaningful bases for \mathcal{E} . Knowing the CSCOs that are available tells the experimenter the possible sets of measurements that can be made to achieve this goal.

We list some CSCOs for specific problems. (table 31 anerson)

1.5 More about operators

1.5.1 Trace of an operator

The trace of an operator A , $\text{Tr}[A]$, is the sum of its diagonal matrix elements:

$$\text{Tr}[A] = \sum_i \langle u_i | A | u_i \rangle, \quad \text{and} \quad \text{Tr}[A] = \int d\alpha \langle \omega_\alpha | A | \omega_\alpha \rangle.$$

The trace is **invariant of the basis**, meaning that a change of representation will not affect the final result.

For a discrete basis, for instance, we have

$$\sum_i \langle u_i | A | u_i \rangle = \sum_i \langle u_i | \left[\sum_k |t_k\rangle \langle t_k| \right] A | u_i \rangle = \sum_{i,j} \langle t_k | A | u_i \rangle \langle u_i | t_k \rangle = \sum_k \langle t_k | A | \mathbb{1} | t_k \rangle = \sum_k \langle t_k | A | t_k \rangle.$$

If A is an observable, then $\text{Tr}[A]$ can be calculated in a basis of eigenvectors of A . The diagonal matrix elements are then the eigenvalues a_n of A and the trace can be written

$$\text{Tr}[A] = \sum_n g_n a_n, \quad g_n = \text{degree of degeneracy of } a_n. \quad (1.97)$$

We list some properties:

$$\text{Tr}[AB] = \text{Tr}[BA] \mid \text{Tr}[ABC] = \text{Tr}[BCA] = \text{Tr}[CAB] \text{ (cyclic permutation)}$$

1.5.2 Function of an operator

To express a function of an operator A , $F(A)$, we use Taylor expansion:

$$F(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(a)}{n!} (x-a)^n = \sum_{n=0}^{\infty} f_n (x-a)^n \Rightarrow F(A) = \sum_{n=0}^{\infty} f_n (A-a)^n. \quad (1.98)$$

For example, the e^A operator around $a = 0$ is:

$$e^A = \sum_{n=0}^{\infty} \frac{A^n}{n!} = \mathbb{1} + A + \frac{A^2}{2!} + \frac{A^3}{3!} + \dots$$

Let $|\varphi_k\rangle$ be an eigenvector of A with eigenvalue λ_k , then (assuming $a = 0$):

$$A|\varphi_k\rangle = \lambda_k|\varphi_k\rangle \implies F(A)|\varphi_k\rangle = \sum_{n=0}^{\infty} f_n A^n \lambda_k |\varphi_k\rangle = \sum_{n=0}^{\infty} f_n \lambda_k^n |\varphi_k\rangle = F(\lambda_k)|\varphi_k\rangle.$$

If the operator A has an eigenpar (λ_k, φ_k) , then $(F(\lambda_k), \varphi_k)$ is the eigenpar of $F(A)$.

Potential operator

The potential operator is a function $V(\cdot)$ with the position operator X as the argument, $V(X)$.

The eigenequation associated to this function is

$$V(\mathbf{R})|\mathbf{r}\rangle = V(\mathbf{r})|\mathbf{r}\rangle. \quad (1.99)$$

The matrix elements in $\{|\mathbf{r}\rangle\}$ are:

$$\langle \mathbf{r}|V(\mathbf{R})|\mathbf{r}'\rangle = V(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}'). \quad (1.100)$$

Finally, using the eigenequation above and the fact that $V(\mathbf{R})$ is Hermitian (the function $V(\mathbf{r})$ is real), we obtain:

$$\langle \mathbf{r}|V(\mathbf{R})|\psi\rangle = V(\mathbf{r})\psi(\mathbf{r}). \quad (1.101)$$

This shows that the action of $V(\mathbf{R})$ is simply multiplication by $V(\mathbf{r})$.

1.5.3 Commutator algebra

We have seen that the commutator of two operators is

$$[A, B] = AB - BA. \quad (1.102)$$

We then present some properties:

| | |
|---|---|
| $[A, B] = -[B, A]$ $[A, B]^\dagger = [B^\dagger, A^\dagger]$ $[F(A), A] = 0$ $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$ $e^A e^B = e^{A+B} e^{\frac{1}{2}[A, B]} \quad ([A, [A, B]] = [B, [A, B]] = 0)$ $[X, P] = i\hbar$ | $[A + B, C + D] = [A, C] + [A, D] + [B, C] + [B, D]$ $[A, BC] = [A, B]C + B[A, C]$ $[A, B] = 0 \implies [F(A), B] = [A, F(B)] = [F(A), F(B)] = 0$ $[A, [A, B]] = [B, [A, B]] = 0 \implies [A, F(B)] = [A, B] \frac{dF(B)}{dB}$ $[A, [A, B]] = [B, [A, B]] = 0 \implies [F(A), B] = [A, B] \frac{dF(A)}{dA}$ |
|---|---|

1.5.4 Derivative of an operator

Let $A(t)$ be a time-dependent operator, whose derivative is dA/dt . In a time-independent basis $\{|u_n\rangle\}$, the matrix elements of A and dA/dt are:

$$A_{ij}(t) = \langle u_i | A | u_j \rangle, \quad \text{and} \quad \left(\frac{dA}{dt} \right)_{ij} = \langle u_i | \frac{dA}{dt} | u_j \rangle = \frac{d}{dt} \langle u_i | A | u_j \rangle = \frac{dA_{ij}}{dt}. \quad (1.103)$$

The last equation corresponds to the matrix elements of dA/dt . We see that,

To obtain the matrix elements of dA/dt , we compute the derivative of each element of A .

Properties of differentiation also apply here. For instance, for product rule we have

$$\begin{aligned} \langle u_i | FG | u_j \rangle &= \sum_k \langle u_i | F | u_k \rangle \langle u_k | G | u_j \rangle \implies \langle u_i | \frac{d(FG)}{dt} | u_j \rangle = \sum_k \left[\langle u_i | \frac{dF}{dt} | u_k \rangle \langle u_k | G | u_j \rangle + \langle u_i | F | u_k \rangle \langle u_k | \frac{dG}{dt} | u_j \rangle \right] \\ &= \langle u_i | \frac{dF}{dt} G + F \frac{dG}{dt} | u_j \rangle. \end{aligned}$$

Other two examples are

$$\frac{d(e^{At})}{dt} = A e^{At} \text{ they commute } \equiv e^{At} A, \quad \text{and} \quad \frac{d(e^{At} e^{Bt})}{dt} = A e^{At} e^{Bt} + e^{At} B e^{Bt}.$$

1.5.5 Unitary operators

An operator U is unitary if its inverse U^{-1} is equal to its adjoint U^\dagger :

$$U^\dagger U = U U^\dagger = \mathbb{1}. \quad (1.104)$$

The scalar product of $|\tilde{\psi}_1\rangle = U|\psi_1\rangle$ and $|\tilde{\psi}_2\rangle = U|\psi_2\rangle$ is conserved with unitary operators:

$$\langle \tilde{\psi}_1 | \tilde{\psi}_2 \rangle = \langle \psi_1 | U^\dagger U | \psi_2 \rangle = \langle \psi_1 | \psi_2 \rangle (= \delta_{ij}).$$

We show some important things about U :

- If A is a Hermitian operator, the operator $T = e^{iA}$ is unitary:

$$T^\dagger T = T T^\dagger = (e^{-iA})(e^{iA}) = \mathbb{1}.$$

- The product of two unitary operators (U, V for instance) is also unitary:

$$(UV)^\dagger (UV) = V^\dagger U^\dagger U V = V^\dagger V = \mathbb{1}.$$

When two transformations conserve the scalar product, so does the successive application of these two transformations.

- Unitary operators constitute the generalization of orthogonal operators to complex spaces.

Change of bases

Lets consider an orthonormal basis $\{|v_i\rangle\}$ and the transformation $\{|\tilde{v}_i\rangle\}$ basis under U , which are also orthonormal.

These vectors constitute a basis of \mathcal{E} , because

$$U^\dagger|\psi\rangle = \sum_i c_i|v_i\rangle / U \longrightarrow UU^\dagger|\psi\rangle = \sum_i c_i U|v_i\rangle = \sum_i c_i|\tilde{v}_i\rangle.$$

Any vector $|\psi\rangle$ can be expanded on the vectors $|\tilde{v}_i\rangle$, which therefore constitutes a basis.

How can one see from the matrix representing U if this operator is unitary?

When a matrix is unitary, the sum of the product of the elements of one column and the complex conjugates of the elements of another column is:

- zero if the two columns are different.
- one if they are not.

Given that $U|\psi_u\rangle = u|\psi_u\rangle$, the square of the norm of $U|\psi_u\rangle$ is:

$$\langle\psi_u|U^\dagger U|\psi_u\rangle = u^*u\langle\psi_u|\psi_u\rangle = u^*u.$$

Since the unitary operator conserves the norm, we have $u^*u = 1$. The eigenvalues of a unitary operator must therefore be complex numbers of modulus 1.

Unitary transformations of operators

A unitary operator U permits the construction, starting from one orthonormal basis $\{|v_i\rangle\} \in \mathcal{E}$, of another one, $\{|\tilde{v}_i\rangle\}$.

Lets define the transform \tilde{A} of the operator A as the operator which, in the $\{|\tilde{v}_i\rangle\}$ basis, has the same matrix elements as A in $\{|v_i\rangle\}$:

$$\langle\tilde{v}_i|\tilde{A}|\tilde{v}_j\rangle = \langle v_i|A|v_j\rangle. \quad (1.105)$$

Using $|\tilde{v}\rangle = U|v\rangle$:

$$\langle v_i|U^\dagger \tilde{A} U|v_j\rangle = \langle v_i|A|v_j\rangle \implies \tilde{A} = UAU^\dagger \quad \text{Definition of } \tilde{A}.$$

This can be taken to be the definition of the transform \tilde{A} of the operator A by the unitary transformation U .

How can the eigenvectors of \tilde{A} be obtained from those of A ?

$$\tilde{A}|\varphi_a\rangle = (UAU^\dagger)U|\varphi_a\rangle = UA(U^\dagger U)|\varphi_a\rangle = UA|\varphi_a\rangle = aU|\varphi_a\rangle = a|\tilde{\varphi}_a\rangle.$$

Eigenpar of the transform \tilde{A}

The eigenvectors of the transform \tilde{A} of A are the transforms $|\tilde{\varphi}_a\rangle$ of eigenvectors $|\varphi_a\rangle$ of A : the eigenvalues are **unchanged**.

- The adjoint of the transform \tilde{A} of A by U is the transform of A^\dagger by U :

$$(\tilde{A})^\dagger = (UAU^\dagger)^\dagger = UA^\dagger U^\dagger = \tilde{A}^\dagger.$$

- Similarly,

$$(\tilde{A})^2 = UAU^\dagger UAU^\dagger = UAAU^\dagger = \tilde{A}^2 \implies (\tilde{A})^n = \tilde{A}^n.$$

Also,

$$\tilde{F}(A) = F(\tilde{A}).$$

1.6 Two important examples of representation and observables

1.6.1 The $\{r\}$ and $\{p\}$ representations

Recall the following bases of \mathcal{F} . They are not composed of functions belonging to \mathcal{F} :

$$\xi_{r_0}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_0) \quad \text{and} \quad v_{p_0}(\mathbf{r}) = (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar} \mathbf{p}_0 \cdot \mathbf{r}} \quad (1.106)$$

Every sufficiently regular equare-integrable function can be expanded in one or the other of these bases. The ket associated with $\xi_{r_0}(\mathbf{r})$ and $v_{p_0}(\mathbf{r})$ will be denoted as:

$$\xi_{r_0}(\mathbf{r}) \iff |\mathbf{r}_0\rangle \quad \text{and} \quad v_{p_0}(\mathbf{r}) \iff |\mathbf{p}_0\rangle. \quad (1.107)$$

Using these bases $\{\xi_{r_0}(\mathbf{r})\}$ and $\{v_{p_0}(\mathbf{r})\}$ of \mathcal{F} we thus define in \mathcal{E}_r two representation: the $\{|\mathbf{r}_0\rangle\}$ and the $\{|\mathbf{p}_0\rangle\}$ representations.

Orthonormalization and closure relations

If we calculate the scalar product of two kets, we have

$$\langle \mathbf{r}_0 | \mathbf{r}'_0 \rangle = \int d^3r \xi_{r_0}^*(\mathbf{r}) \xi_{r'_0}(\mathbf{r}) = \delta(\mathbf{r}_0 - \mathbf{r}'_0) \quad \text{and} \quad \langle \mathbf{p}_0 | \mathbf{p}'_0 \rangle = \int d^3r v_{p_0}^*(\mathbf{r}) v_{p'_0}(\mathbf{r}) = \delta(\mathbf{p}_0 - \mathbf{p}'_0).$$

Thus, the bases are therefore orthonormal in the extended sense. The fact that the set of the $|\mathbf{r}_0\rangle$ or that of $|\mathbf{p}_0\rangle$ constitutes a basis in \mathcal{E}_r can be expressed by a closure relation in \mathcal{E}_r :

$$\text{Orthonormality relation} \quad \text{Closure relation} \quad (1.108)$$

$$\begin{aligned} \langle \mathbf{r}_0 | \mathbf{r}'_0 \rangle &= \delta(\mathbf{r}_0 - \mathbf{r}'_0) \\ \langle \mathbf{p}_0 | \mathbf{p}'_0 \rangle &= \delta(\mathbf{p}_0 - \mathbf{p}'_0) \end{aligned}$$

$$\begin{aligned} \int d^3r_0 |\mathbf{r}_0\rangle \langle \mathbf{r}_0| &= \mathbb{1} \\ \int d^3p_0 |\mathbf{p}_0\rangle \langle \mathbf{p}_0| &= \mathbb{1} \end{aligned} \quad (1.109)$$

Components of a ket

Consider a ket $|\psi\rangle$ corresponding to $\psi(\mathbf{r})$. We can expand it in each representation using the closure relation:

$$|\psi\rangle = \int d^3r_0 |\mathbf{r}_0\rangle \langle \mathbf{r}_0|\psi\rangle, \quad \text{where} \quad \langle \mathbf{r}_0|\psi\rangle = \psi(\mathbf{r}_0) = \int d^3r \xi_{\mathbf{r}_0}^*(\mathbf{r}) \psi(\mathbf{r}). \quad (1.110)$$

$$|\psi\rangle = \int d^3p_0 |\mathbf{p}_0\rangle \langle \mathbf{p}_0|\psi\rangle, \quad \text{where} \quad \langle \mathbf{p}_0|\psi\rangle = \tilde{\psi}(\mathbf{p}_0) = \int d^3r v_{\mathbf{p}_0}^*(\mathbf{r}) \psi(\mathbf{r}). \quad (1.111)$$

We see that $\tilde{\psi}(\mathbf{p}_0)$ is the Fourier transform of $\psi(\mathbf{r}_0)$. Each value corresponds to the components of $|\psi\rangle$ on the basis vector of the respective representation.

Now, we redefine the above bases to just $|\mathbf{r}\rangle$ and $|\mathbf{p}\rangle$:

$$\begin{aligned} \langle \mathbf{r}|\psi\rangle &= \psi(\mathbf{r}) & \langle \mathbf{p}|\psi\rangle &= \tilde{\psi}(\mathbf{p}) \\ \langle \mathbf{r}|\mathbf{r}'\rangle &= \delta(\mathbf{r} - \mathbf{r}') & \langle \mathbf{p}|\mathbf{p}'\rangle &= \delta(\mathbf{p} - \mathbf{p}') \\ \int d^3r |\mathbf{r}\rangle \langle \mathbf{r}| &= \mathbb{1} & \int d^3p |\mathbf{p}\rangle \langle \mathbf{p}| &= \mathbb{1} \end{aligned} \quad (1.112)$$

Changing from $\{|\mathbf{r}\rangle\}$ to $\{|\mathbf{p}\rangle\}$ representation

Changing from one basis to the other brings in the numbers:

$$\langle \mathbf{r}|\mathbf{p}\rangle = \langle \mathbf{p}|\mathbf{r}\rangle^* = \int d^3r' \langle \mathbf{r}|\mathbf{r}'\rangle \langle \mathbf{r}'|\mathbf{p}\rangle = \int d^3r' \delta(\mathbf{r} - \mathbf{r}') (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}'} = (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}}. \quad (1.113)$$

A given ket $|\psi\rangle$ is represented by $\langle \mathbf{r}|\psi\rangle = \psi(\mathbf{r})$ in the $\{|\mathbf{r}\rangle\}$ representation and by $\langle \mathbf{p}|\psi\rangle = \tilde{\psi}(\mathbf{p})$ in the $\{|\mathbf{p}\rangle\}$ representation.

Therefore,

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle = \int d^3p \langle \mathbf{r}|\mathbf{p}\rangle \langle \mathbf{p}|\psi\rangle = (2\pi\hbar)^{-3/2} \int d^3p e^{\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \tilde{\psi}(\mathbf{p}) \quad (1.114)$$

$$\tilde{\psi}(\mathbf{p}) = \langle \mathbf{p}|\psi\rangle = \int d^3r \langle \mathbf{p}|\mathbf{r}\rangle \langle \mathbf{r}|\psi\rangle = (2\pi\hbar)^{-3/2} \int d^3r e^{-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}} \psi(\mathbf{r}) \quad (1.115)$$

$$A(\mathbf{p}, \mathbf{p}') = (2\pi\hbar)^{-3} \int d^3r \int d^3r' e^{\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - \mathbf{p}'\cdot\mathbf{r}')} A(\mathbf{r}', \mathbf{r}) \quad (1.116)$$

1.6.2 The R and P operators

We define the X , Y , Z operators whose action, in the $\{|\mathbf{r}\rangle\}$ representation, is given by:

$$\begin{aligned} \langle \mathbf{r}|X|\psi\rangle &= x \langle \mathbf{r}|\psi\rangle \\ \langle \mathbf{r}|Y|\psi\rangle &= y \langle \mathbf{r}|\psi\rangle \\ \langle \mathbf{r}|Z|\psi\rangle &= z \langle \mathbf{r}|\psi\rangle \end{aligned} \quad (1.117)$$

X , Y , and Z will be considered to be the components of a vector operator \mathbf{R} . Similarly, we define the vector operator \mathbf{P} by its components P_x , P_y , P_z , whose action, in the $\{|\mathbf{p}\rangle\}$ representation is given by:

$$\begin{aligned} \langle \mathbf{p}|P_x|\psi\rangle &= p_x \langle \mathbf{p}|\psi\rangle \\ \langle \mathbf{p}|P_y|\psi\rangle &= p_y \langle \mathbf{p}|\psi\rangle \\ \langle \mathbf{p}|P_z|\psi\rangle &= p_z \langle \mathbf{p}|\psi\rangle \end{aligned} \quad (1.118)$$

How \mathbf{P} operator acts in the $\{|\mathbf{r}\rangle\}$ representation? We use the closure relation to obtain:

$$\begin{aligned}\langle \mathbf{r} | P_x | \psi \rangle &= \int d^3p \langle \mathbf{r} | \mathbf{p} \rangle \langle \mathbf{p} | P_x | \psi \rangle \\ &\stackrel{(a)}{=} (2\pi\hbar)^{-3/2} \int d^3p e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} p_x \tilde{\psi}(\mathbf{p}) \\ \langle \mathbf{r} | P_x | \psi \rangle &\stackrel{(b)}{=} \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(\mathbf{r}).\end{aligned}$$

In (a) we have used the equation (1.113) while in (b) we have used the property of the derivative of a Fourier transform. Generally, the result is:

$$\langle \mathbf{r} | \mathbf{P} | \psi \rangle = \frac{\hbar}{i} \nabla \langle \mathbf{r} | \psi \rangle = \frac{\hbar}{i} \nabla \psi(\mathbf{r}). \quad (1.119)$$

In the $\{|bR\rangle\}$ representation, the \mathbf{P} operator coincides with the differential operator $(\hbar/i)\nabla$ applied to the wave functions.

If we compute the commutator say, $[X, P_x]$, we have

$$\begin{aligned}\langle \mathbf{r} | [X, P_x] | \psi \rangle &= \langle \mathbf{r} | (X P_x - P_x X) | \psi \rangle \\ &= \langle \mathbf{r} | X P_x | \psi \rangle - \langle \mathbf{r} | P_x X | \psi \rangle \\ &= \int d^3r' \langle \mathbf{r} | X | \mathbf{r}' \rangle \langle \mathbf{r}' | P_x | \psi \rangle - \int d^3r' \langle \mathbf{r} | P_x | \mathbf{r}' \rangle \langle \mathbf{r}' | X | \psi \rangle \\ &= \int d^3r' [x' \delta(\mathbf{r} - \mathbf{r}')] \frac{\hbar}{i} \frac{\partial}{\partial x} \langle \mathbf{r}' | \psi \rangle - \int d^3r' \left[\frac{\hbar}{i} \frac{\partial}{\partial x} \delta(\mathbf{r} - \mathbf{r}') \right] x' \langle \mathbf{r}' | \psi \rangle \\ &= \frac{\hbar}{i} x \frac{\partial}{\partial x} \langle \mathbf{r} | \psi \rangle - \frac{\hbar}{i} \frac{\partial}{\partial x} (x \langle \mathbf{r} | \psi \rangle) \\ &= \frac{\hbar}{i} x \frac{\partial}{\partial x} \langle \mathbf{r} | \psi \rangle - \frac{\hbar}{i} \langle \mathbf{r} | \psi \rangle - \frac{\hbar}{i} x \frac{\partial}{\partial x} \langle \mathbf{r} | \psi \rangle \\ \langle \mathbf{r} | [X, P_x] | \psi \rangle &= i\hbar \langle \mathbf{r} | \psi \rangle.\end{aligned}$$

Thus, one finds $[X, P_x] = i\hbar$. In the same way, we find all the other commutators between the components of \mathbf{R} and \mathbf{P} :

$$\text{Canonical commutation relations} \quad [R_i, R_j] = 0, \quad [P_i, P_j] = 0, \quad [R_i, P_j] = i\hbar \delta_{ij}, \quad i, j = 1, 2, 3. \quad (1.120)$$

R and P are Hermitian

All the components of \mathbf{R} and \mathbf{P} are Hermitian operators.

For example,

$$\langle \varphi | X | \psi \rangle = \int d^3r \varphi^*(\mathbf{r}) x \psi(\mathbf{r}) = \left[\int d^3r \varphi(\mathbf{r}) x \psi^*(\mathbf{r}) \right]^* = \langle \psi | X | \varphi \rangle^*.$$

Eigenvectors of R and P

Consider the action of X on the ket $|\mathbf{r}_0\rangle$:

$$\langle \mathbf{r} | X | \mathbf{r}_0 \rangle = x \langle \mathbf{r} | \mathbf{r}_0 \rangle = x \delta(\mathbf{r} - \mathbf{r}_0) = x_0 \delta(\mathbf{r} - \mathbf{r}_0) = x_0 \langle \mathbf{r} | \mathbf{r}_0 \rangle.$$

The components in $\{|\mathbf{r}\rangle\}$ representation of the ket $X|\mathbf{r}_0\rangle$ are equal to those of the ket \mathbf{r}_0 multiplied by x_0 :

$$X|\mathbf{r}_0\rangle = x_0|\mathbf{r}_0\rangle. \quad (1.121)$$

Omitting the index zero, and doing the same for the other components of \mathbf{R} and \mathbf{P} in their respective representations yield:

$$\begin{array}{l} X|\mathbf{r}\rangle = x|\mathbf{r}\rangle \\ Y|\mathbf{r}\rangle = y|\mathbf{r}\rangle \\ Z|\mathbf{r}\rangle = z|\mathbf{r}\rangle \end{array}, \quad \text{and} \quad \begin{array}{l} P_x|\mathbf{p}\rangle = p_x|\mathbf{p}\rangle \\ P_y|\mathbf{p}\rangle = p_y|\mathbf{p}\rangle \\ P_z|\mathbf{p}\rangle = p_z|\mathbf{p}\rangle \end{array} \quad (1.122)$$

R and P are observables

We have already demonstrated the closure relation for each representation $\{|\mathbf{r}\rangle\}$ and $\{|\mathbf{p}\rangle\}$ in equation (1.112). Therefore, \mathbf{R} and \mathbf{P} are observables. In a three-dimensional space, is necessary to specify the eigenvalues x_o, y_o, z_o as they uniquely determines the corresponding eigenvector $|\mathbf{r}_0\rangle$.

The set of the three operators X, Y, Z and the set of the three operators P_x, P_y, P_z constitute a CSCO in $\mathcal{E}_{\mathbf{r}}$.

Recall that an operator must have eigenvectors that span the whole state vector, so missing one coordinate will degenerate it and therefore is no longer uniquely determined. One can also mix X with P as $\{X, P_y, P_z\}$ to create CSCOs.

Chapter 2

Postulates of Quantum Mechanics

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2.1 Introduction

In classical mechanics, the motion of any physical system is determined through the position $\mathbf{r} = (x, y, z)$ and the velocity $\mathbf{v} = (\dot{x}, \dot{y}, \dot{z})$. One usually introduces generalized coordinates $q_i(t)$ whose derivatives with respect to time $\dot{q}_i(t)$ are the generalized velocities. With these coordinates, the position and velocity of any point can be calculated. Using the Lagrangian $\mathcal{L}(q_i, \dot{q}_i, t)$ one defines the conjugate momentum p_i of each of the generalized coordinates q_i :

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}.$$

The $q_i(t)$ and $p_i(t)$ are called **fundamental dynamical variables**. All the physical quantities associated with the system (energy, angular momentum, etc) can be expressed in terms of the fundamental dynamical variables.

The motion (evolution) of a system can be studied by Lagrange's equations or the Hamilton-Jacobi canonical equation:

$$\text{Hamilton-Jacobi equations} \quad \frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i}, \quad \text{and} \quad \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i}.$$

The classical description of a physical system can be summarized as follows:

- The state of the system at time t_0 is defined by specifying N generalized coordinates $q_i(t_0)$ and their N conjugate momenta $p_i(t_0)$.
- Knowing the state of the system at t_0 , allows to predict with certainty the result of any measurement performed at time t_0 .
- The time evolution of the state of the system is given by the **Hamilton-Jacobi** equations. The state of the system is known for all time if its initial state is known.

2.2 Statements of the postulates

2.2.1 State and measurable physical quantities of a system

The quantum state of a particle at a fixed time is characterized by a ket of the space \mathcal{E}_r .

First postulate: State of a system

At time t_0 , the state of an isolated physical system is defined by specifying a ket $|\psi(t_0)\rangle \in \mathcal{E}_r$.

Recall that, since \mathcal{E} is a vector space, a linear combination of state vectors is a state vector.

Second postulate: Measurable physical quantities

Every measurable physical quantity \mathcal{A} is described by an operator A acting in \mathcal{E} : this operator is an **observable**.

In this sense, a state is represented by a vector, while a physical quantity by an operator.

Third postulate: Outcomes of measurements

The only possible result of the measurement of a physical quantity \mathcal{A} is one of the eigenvalues of the corresponding observable A .

- A measurement of \mathcal{A} gives **always** a real value, since A is Hermitian by definition.
- If the spectrum of A is discrete, the results that can be obtained by measuring \mathcal{A} are **quantized**.

2.2.2 Principle of spectral decomposition

Consider a system whose state is characterized, at a given time, by $|\psi\rangle$, which is assumed normalized. We want to predict the result of the measurement, at this time, of a physical quantity \mathcal{A} associated with the observable A .

Discrete spectrum

If all eigenvalues a_n of A are non-degenerate, there is associated with each of them a **unique** eigenvector $|u_n\rangle$. As A is an observable, the set of $|u_n\rangle$ which we assume normalized, constitutes a basis in \mathcal{E} and we can expand $|\psi\rangle$:

$$A|u_n\rangle = a_n|u_n\rangle \implies |\psi\rangle = \sum_n c_n|u_n\rangle$$

The probability $P(a_n)$ of finding a_n when \mathcal{A} is measured is therefore:

$$P(a_n) = |c_n|^2 = |\langle u_n|\psi\rangle|^2.$$

If, however, some of the eigenvalues a_n are degenerate, several orthonormalized eigenvectors $|u_n^i\rangle$ corresponds to them and we can still expand $|\psi\rangle$ on the orthonormal basis $\{|u_n^i\rangle\}$:

$$A|u_n^i\rangle = a_n|u_n^i\rangle, \quad i = 1, 2, \dots, g_n \implies |\psi\rangle = \sum_n \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle. \quad (2.1)$$

The probability now becomes

$$P(a_n) = \sum_{i=1}^{g_n} |c_n^i|^2 = \sum_{i=1}^{g_n} |\langle u_n^i|\psi\rangle|^2. \quad (2.2)$$

Fourth postulate (discrete case): Result of a measurement

When \mathcal{A} is measured on a system in the normalized state $|\psi\rangle$, the probability $P(a_n)$ of obtaining the eigenvalue a_n of the observable A is the discrete projection of ψ onto the eigensubspace \mathcal{E}_n :

$$P(a_n) = \langle \psi | P_n | \psi \rangle = \sum_{i=1}^{g_n} |\langle u_n^i | \psi \rangle|^2, \quad P_n = \sum_{i=1}^{g_n} |u_n^i\rangle \langle u_n^i|.$$

$\{|u_n^i\rangle\}$ is a set of orthonormal vectors which forms a basis in the eigensubspace \mathcal{E}_n .

Continuous case

If now the spectrum of A is continuous and non-degenerate, the eigenvectors of A forms a continuous basis in \mathcal{E} , in terms of which $|\psi\rangle$ can be expanded:

$$A|v_\alpha\rangle = \alpha|v_\alpha\rangle \implies |\psi\rangle = \int d\alpha c(\alpha)|v_\alpha\rangle.$$

In this case, we cannot define the probability on a single point; we must define a probability density function. The differential probability of obtaining a value included between α and $\alpha + d\alpha$ is

$$dP(\alpha) = \rho(\alpha)d\alpha, \quad \text{with} \quad \rho(\alpha) = |c(\alpha)|^2 = |\langle v_\alpha|\psi\rangle|^2.$$

Fourth postulate (continuous case, non-degenerate): Result of a measurement

If \mathcal{A} is measured in the normalized state $|\psi\rangle$, the probability of obtaining a result within between α_1 and α_2 is the continuous projection of ψ onto that interval:

$$P(\alpha_1 < \alpha < \alpha_2) = \langle \psi | P_{\alpha_1, \alpha_2} | \psi \rangle = \int_{\alpha_1}^{\alpha_2} |\langle v_\alpha | \psi \rangle|^2 d\alpha, \quad P_{\alpha_1, \alpha_2} = \int_{\alpha_1}^{\alpha_2} |v_\alpha\rangle \langle v_\alpha| d\alpha. \quad (2.3)$$

In cases where the state $|\psi\rangle$ is **not normalized**, we then use the following expressions:

$$\begin{array}{ll} \text{Discrete case} & \text{Continuous case} \\ P(a_n) = \frac{1}{\langle \psi | \psi \rangle} \sum_{i=1}^{g_n} |c_n^i|^2 & \rho(\alpha) = \frac{1}{\langle \psi | \psi \rangle} |c(\alpha)|^2. \end{array} \quad (2.4)$$

On the other hand, two proportional state vectors, $|\psi'\rangle = ae^{i\theta}|\psi\rangle$, represent **the same** physical state:

$$|\langle u_n^i | \psi' \rangle|^2 = |e^{i\theta} \langle u_n^i | \psi \rangle|^2 = |\langle u_n^i | \psi \rangle|^2.$$

a is simplified when dividing by $\langle \psi' | \psi' \rangle$.

Global versus relative phase factor

A global phase factor does not affect the physical predictions, but the relative phases of the coefficients of an expansion are significant.

2.2.3 Reduction of the wave packet

We want to measure at a given point the physical quantity \mathcal{A} . If the ket $|\psi\rangle$ before the measurement is known, the fourth postulate allows us to predict the probability of the various possible outcomes. Immediately after the measurement, we cannot speak of probability, as we have already got the result (collapse).

If the measurement of \mathcal{A} resulted in a_n (assuming discrete spectrum of A), the state of the system immediately after this measurement is the eigenvector $|u_n\rangle$ associated with a_n :

$$\text{State of collapse} \quad |\psi\rangle \xrightarrow{(a_n)} |u_n\rangle. \quad (2.5)$$

- If we perform a second measurement of \mathcal{A} immediately after the first one, we shall always find the same result a_n .
- We use just after the measurement to assume the system had not time to evolve, because otherwise the state evolves and we need the sixth postulate to keep track of this motion.

When the eigenvalue a_n is degenerate, then the state just before the measurement is written as (equation (2.1)):

$$|\psi\rangle = \sum_n \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle.$$

And the state of collapse just after the measurement is

$$\text{State of collapse} \quad |\psi\rangle \xrightarrow{(a_n)} \frac{1}{\sqrt{\sum_{i=1}^{g_n} |c_n^i|^2}} \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle. \quad (2.6)$$

The square root factor is the normalization so that we get a unitary norm of the state. We rewrite the above expression in the following fifth postulate.

Fifth postulate: State of collapse

If the measurement of the \mathcal{A} in the state $|\psi\rangle$ gives the result a_n , the state of the system immediately after the measurement is the normalized projection of $|\psi\rangle$ onto the eigensubspace \mathcal{E}_n associated with a_n :

$$|\psi\rangle \xrightarrow{(a_n)} \frac{P_n |\psi\rangle}{\sqrt{\langle \psi | P_n | \psi \rangle}} \quad (2.7)$$

It is not an arbitrary ket of \mathcal{E}_n , but the part of $|\psi\rangle$ that belongs to \mathcal{E}_n .

2.2.4 Time evolution of Systems

Sixth postulate: Time evolution of the system

The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrodinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle, \quad (2.8)$$

where $H(t)$ is the **Hamiltonian operator** (observable) associated with the total energy of the system.

2.2.5 Quantization rules

We will discuss how to construct, for a physical quantity \mathcal{A} already defined in classical mechanics, the operator A which describes it in quantum mechanics.

2.3 The physical interpretation of the postulates

2.3.1 Quantization rules are consistent with probabilistic interpretation

Lets consider a one-dimensional problem. If the particle is in the normalized state $|\psi\rangle$, the probability that a measurement of its position will yield a result included between x and $x + dx$ is equal to (equation (2.4)):

$$dP(x) = |\langle x|\psi\rangle|^2 dx.$$

Now, to the eigenvector $|p\rangle$ of the observable P corresponds the plane wave:

$$\langle x|p\rangle = (2\pi\hbar)^{-1/2} e^{\frac{ipx}{\hbar}}. \quad (2.9)$$

and we have seen that de Broglie relations associate with this wave a well-defined momentum which is precisely p . In addition, the probability of finding, for a particle in $|\psi\rangle$, a momentum between p and $p + dp$ is:

$$dP(p) = |\langle p|\psi\rangle|^2 dp = |\tilde{\psi}(p)|^2 dp. \quad (2.10)$$

2.3.2 The measurement process

There is the question of the "fundamental" perturbation involved in the observation of quantum system. The origin of these problems lies in the fact that the system under study is treated independently from the measurement device, although their interaction is essential to the observation process. One should actually consider the system and the measurement device together as a whole. This raises delicate questions concerning the details of the measurement process.

The nondeterministic formulation of the fourth and fifth postulates is related to the problems that we have mentioned. Of course, the abrupt change from one state vector to another due to the measurement corresponds to the fundamental perturbation of which we have spoken. We shall consider here only ideal measurements: the perturbation they provoke is due only to the quantum mechanical aspect of the measurement. Of course, real devices always present imperfections that affect the measurement and the system.

2.3.3 Mean value of an observable in a given state

The predictions deduced from the fourth postulate are expressed in terms of probabilities. To verify them, it would be necessary to perform a large number of measurements under identical conditions. This means measuring the same quantity in a large number of systems which are all in the same quantum state. If these predictions are correct, the proportion of N identical experiments resulting in a given event will approach, as $N \rightarrow \infty$, the theoretically predicted probability P of this event. In practice, of course, N is finite, and statistical techniques must be used to interpret the results.

The **mean value of an observable** A in the state $|\psi\rangle$, which we shall denote by $\langle A \rangle_\psi$, or $\langle A \rangle$, is defined as the average of the results obtained when a large number N of measurements of this observable are performed on systems which are all in the state $|\psi\rangle$. When $|\psi\rangle$ is given, we can compute the probabilities of finding all the possible results, and therefore, $\langle A \rangle_\psi$ is known.

If $|\psi\rangle$ is normalized, $\langle A \rangle$ is given by

$$\langle A \rangle_\psi = \langle \psi|A|\psi \rangle \quad (2.11)$$

Assuming discrete spectrum, out of N measurements of \mathcal{A} , the eigenvalue a_n will be obtained $N(a_n)$ times, with

$$\lim_{N \rightarrow \infty} \frac{N(a_n)}{N} = P(a_n), \quad \text{and} \quad \sum_n N(a_n) = N. \quad (2.12)$$

In the limit, we can approximate therefore the mean value of the results as

$$\langle A \rangle_\psi = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_n a_n N(a_n) = \sum_n a_n P(a_n). \quad (2.13)$$

The last expression is then treated:

$$\begin{aligned} \langle A \rangle_\psi &= \sum_n a_n P(a_n) = \sum_n a_n \langle \psi | P_n | \psi \rangle = \sum_n a_n \sum_{i=1}^{g_n} \langle \psi | u_n^i \rangle \langle u_n^i | \psi \rangle = \sum_n \sum_{i=1}^{g_n} \langle \psi | a_n | u_n^i \rangle \langle u_n^i | \psi \rangle \\ &= \sum_n \sum_{i=1}^{g_n} \langle \psi | A | u_n^i \rangle \langle u_n^i | \psi \rangle = \langle \psi | A \left[\sum_n \sum_{i=1}^{g_n} | u_n^i \rangle \langle u_n^i | \right] | \psi \rangle = \langle \psi | A \mathbf{1} | \psi \rangle = \langle \psi | A | \psi \rangle. \end{aligned}$$

In the continuous case, we have something similar:

$$\lim_{N \rightarrow \infty} \frac{dN(\alpha)}{N} = dP(\alpha). \quad (2.14)$$

In the limit, we can approximate the mean value of the results as

$$\langle A \rangle_\psi = \lim_{N \rightarrow \infty} \frac{1}{N} \int \alpha dN(\alpha) = \int \alpha dP(\alpha). \quad (2.15)$$

The last expression is then treated:

$$\begin{aligned} \langle A \rangle_\psi &= \int \alpha dP(\alpha) = \int \alpha \langle \psi | v_\alpha \rangle \langle v_\alpha | \psi \rangle d\alpha = \int \langle \psi | A | v_\alpha \rangle \langle v_\alpha | \psi \rangle d\alpha \\ &= \langle \psi | A \left[\int d\alpha | v_\alpha \rangle \langle v_\alpha | \right] | \psi \rangle = \langle \psi | A \mathbf{1} | \psi \rangle = \langle \psi | A | \psi \rangle. \end{aligned}$$

- If the ket $|\psi\rangle$ is not normalized, then we use

$$\text{Mean value of } A \quad \langle A \rangle_\psi = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (2.16)$$

- In practice, one often places oneself in a particular representation to compute $\langle A \rangle_\psi$.

$$\begin{aligned} \langle X \rangle_\psi &= \langle \psi | X | \psi \rangle = \int d^3r \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | X | \psi \rangle = \int d^3r \psi^*(\mathbf{r}) x \psi(\mathbf{r}). \\ \langle P_x \rangle_\psi &= \langle \psi | P_x | \psi \rangle = \int d^3r \tilde{\psi}^*(\mathbf{p}) p_x \tilde{\psi}(\mathbf{p}), \quad \text{or} \\ \langle P_x \rangle_\psi &= \langle \psi | P_x | \psi \rangle = \int d^3r \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | P_x | \psi \rangle = \int d^3r \psi^*(\mathbf{r}) \left[\frac{\hbar}{i} \frac{\partial}{\partial x} \psi(\mathbf{r}) \right]. \end{aligned}$$

2.3.4 The root mean square deviation

$\langle A \rangle$ indicates the order of magnitude of the values of the observables A when the system is in the state $|\psi\rangle$. However, this mean values does not give any idea of the dispersion of the results we expect when measuring A .

We therefore define the **root mean square deviation** ΔA as

$$\text{RMS deviation} \quad \Delta A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}. \quad (2.17)$$

If this definition is applied to the observable R and P , we can shown, using commutation realtions, that for any state $|\psi\rangle$, we have

$$\begin{aligned} \Delta X \cdot \Delta P_x &\geq \frac{\hbar}{2} \\ \Delta Y \cdot \Delta P_y &\geq \frac{\hbar}{2} \\ \Delta Z \cdot \Delta P_z &\geq \frac{\hbar}{2} \end{aligned} \quad \text{Heisenberg relations} \quad (2.18)$$

2.3.5 Compatibility of observables

Compatibility and commutation rules

Let be two commute observable A and B $[A, B] = 0$, and assume discrete spectrum. There exists a basis of the state space composed of eigenkets commont to A and B , which we denote $|a_n, b_p, i\rangle$:

$$\begin{aligned} A|a_n, b_p, i\rangle &= a_n|a_n, b_p, i\rangle \\ B|a_n, b_p, i\rangle &= b_p|a_n, b_p, i\rangle. \end{aligned}$$

For any a_n and b_p , there exists at least one state $|a_n, b_p, i\rangle$ for which a measurement of A will always give a_n and a measurement of B will always give b_p . These observables which can be simultaneously determined are said to be **compatible**.

The initial state of a system $|\psi\rangle$ can always be written as

$$|\psi\rangle = \sum_{n,p,i} c_{n,p,i} |a_n, b_p, i\rangle.$$

Assume we measure A and then immediately we measure B . First, the probability of having a_n is

$$P(a_n) = \sum_{p,i} |c_{n,p,i}|^2. \quad (2.19)$$

When we then measure B , the system is no long in the state $|\psi\rangle$ but, if we found a_n in the state $|\psi'_n\rangle$ we have

$$|\psi'_n\rangle = \frac{1}{\sqrt{\sum_{p,i} |c_{n,p,i}|^2}} \sum_{p,i} c_{n,p,i} |a_n, b_p, i\rangle.$$

The probability of obtaining b_p when it is known that the first measurement was a_n is then

$$P_{a_n}(b_p) = \frac{1}{\sum_{p,i} |c_{n,p,i}|^2} \sum_i |c_{n,p,i}|^2. \quad (2.20)$$

The probability $P(a_n, b_p)$ of obtaining a_n in the first measurement and b_p in the second is then a composite event, we must first find a_n and then find b_p . Therefore,

$$P(a_n, b_p) = P(a_n)P_{a_n}(b_p) = \sum_i |c_{n,p,i}|^2. \quad (2.21)$$

The state of the system becomes immediately after the second measurement

$$|\psi''_{n,p}\rangle = \frac{1}{\sqrt{\sum_i |c_{n,p,i}|^2}} \sum_i c_{n,p,i} |a_n, b_p, i\rangle. \quad (2.22)$$

$|\psi''_{n,p}\rangle$ is an eigenvector common to A and B with the eigenvalues a_n and b_p , respectively.

If we do the same in opposite order, that is, measuring B and then A we have

$$P(b_p, a_n) = \sum_i |c_{n,p,i}|^2, \quad \text{and} \quad |\psi''_{p,n}\rangle = \frac{1}{\sqrt{\sum_i |c_{n,p,i}|^2}} \sum_i c_{n,p,i} |a_n, b_p, i\rangle. \quad (2.23)$$

Consequence of compatible observables

When two observables are compatible, the physical predictions are the **same**, whatever the order of performing the two measurements. The probability and the state after the last measurements are for both cases:

$$P(a_n, b_p) = P(b_p, a_n) = \sum_i |c_{n,p,i}|^2 = \sum_i |\langle a_n, b_p, i | \psi \rangle|^2, \quad \text{and} \quad (2.24)$$

$$|\psi''_{n,p}\rangle = |\psi''_{p,n}\rangle = \frac{1}{\sqrt{\sum_i |c_{n,p,i}|^2}} \sum_i c_{n,p,i} |a_n, b_p, i\rangle. \quad (2.25)$$

When two observables A and B are compatible, the measurement of B does not cause any loss of information previously obtained from the measurement of A , and viceversa.

New measurement of A or B will yield the same values again without fail.

Preparation of a state

2.4 Physical implications of the Schrodinger equation

Recall the Schrodinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi\rangle. \quad (2.26)$$

2.4.1 General properties of the Schrodinger equation

There is no indeterminacy in the time evolution of a quantum system. Indeterminacy appears only when a physical quantity is measured.

Between two measurements, the state vectors evolves (following Shrodinger equation) in a perfectly deterministic way.

Supeorposition

The equation (2.26) is linear and homogeneous, then their slutions are linearly superposable:

$$|\psi(t_0)\rangle = \lambda_1|\psi_1(t_0)\rangle + \lambda_2|\psi_2(t_0)\rangle \implies |\psi(t)\rangle = \lambda_1|\psi_1(t)\rangle + \lambda_2|\psi_2(t)\rangle. \quad (2.27)$$

Conservation of probability

Since the Hamiltonian operator $H(t)$ is Hermitian, the square of the norm of the state vector $\langle\psi(t)|\psi(t)\rangle$ does not depend on time:

$$\begin{aligned} \frac{d}{dt}\langle\psi(t)|\psi(t)\rangle &= \left[\frac{d}{dt}\langle\psi(t)| \right] |\psi(t)\rangle + \langle\psi(t)| \left[\frac{d}{dt}|\psi(t)\rangle \right] \\ &= \left[-\frac{1}{i\hbar}\langle\psi(t)|H(t) \right] |\psi(t)\rangle + \langle\psi(t)| \left[\frac{1}{i\hbar}H(t)|\psi(t)\rangle \right] \\ &= -\frac{1}{i\hbar}\langle\psi(t)|H(t)|\psi(t)\rangle + \frac{1}{i\hbar}\langle\psi(t)|H(t)|\psi(t)\rangle \\ \frac{d}{dt}\langle\psi(t)|\psi(t)\rangle &= 0. \end{aligned}$$

The property of conservation of the norm which we have derived is expressed by the equation

$$\langle\psi(t)|\psi(t)\rangle = \int d^3r |\psi(\mathbf{r}, t)|^2 = \langle\psi(t_0)|\psi(t_0)\rangle = 1. \quad (2.28)$$

This implies that time evolution does not modify the global probability of finding the particle in all space, which always remains equal to 1.

Evolution of the mean value of an observable

The mean value of the observable A at the instant t is

$$\langle A \rangle(t) = \langle\psi(t)|A|\psi(t)\rangle. \quad (2.29)$$

The mean value may depends on time by the state $\psi(t)$, but also by the observator itself $A(t)$. If we differentiate the above equation with time we have

$$\begin{aligned} \frac{d}{dt}\langle\psi(t)|A(t)|\psi(t)\rangle &= \left[\frac{d}{dt}\langle\psi(t)| \right] A(t)|\psi(t)\rangle + \langle\psi(t)|A \left[\frac{d}{dt}|\psi(t)\rangle \right] + \langle\psi(t)| \frac{\partial A}{\partial t} |\psi(t)\rangle \\ &= \frac{1}{i\hbar}\langle\psi(t)|[A(t)H(t) - H(t)A(t)]|\psi(t)\rangle + \langle\psi(t)| \frac{\partial A}{\partial t} |\psi(t)\rangle. \end{aligned}$$

Therefore,

$$\text{Evolution of the mean value of } A \quad \frac{d}{dt}\langle A \rangle = \frac{1}{i\hbar}\langle[A, H(t)]\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle. \quad (2.30)$$

The mean value $\langle A \rangle$ is a number which depends only on time t . It is this value that must be compared to the value taken on by the classical quantity $\mathcal{A}(\mathbf{r}, \mathbf{p}, t)$.

We can apply the equation (2.30) to the observables \mathbf{R} and \mathbf{P} , assuming a scalar stationary potential $V(\mathbf{r})$:

$$H = \frac{\mathbf{P}^2}{2m} + V(\mathbf{R}).$$

We also have

$$\frac{d}{dt}\langle \mathbf{R} \rangle = \frac{1}{i\hbar}\langle [\mathbf{R}, H] \rangle = \frac{1}{\hbar}\langle [\mathbf{R}, \frac{\mathbf{P}^2}{2m}] \rangle = \frac{i\hbar}{m}\mathbf{P}, \quad \text{and} \quad \frac{d}{dt}\langle \mathbf{P} \rangle = \frac{1}{i\hbar}\langle [\mathbf{P}, H] \rangle = \frac{1}{i\hbar}\langle [\mathbf{P}, V(\mathbf{R})] \rangle = -i\hbar\nabla V(\mathbf{R}).$$

Therefore, we have the **Ehrenfest's theorem**:

$$\text{Ehrenfest's theorem} \quad \begin{aligned} \frac{d}{dt}\langle \mathbf{R} \rangle &= \frac{1}{m}\langle \mathbf{P} \rangle \\ \frac{d}{dt}\langle \mathbf{P} \rangle &= -\langle \nabla V(\mathbf{R}) \rangle \end{aligned} \quad (2.31)$$

classical limits of the Ehrenfest's theorem

2.4.2 Conservative systems

When the Hamiltonian of a physical system **does not** depend explicitly on time, the system is said to be **conservative**. It can also be said that the total energy of the system is constant of the motion.

Solution of the Schrodinger equation

Lets consider the eigenequation of H (assuming discrete spectrum):

$$H|\varphi_{n,\tau}\rangle = E_n|\varphi_{n,\tau}\rangle. \quad (2.32)$$

τ is used to denote the set of indices other than n necessary to uniquely characterizes a unique vector $|\varphi_{n,\tau}\rangle$. Since H does not depend on time, neither E_n nor $|\varphi_{n,\tau}\rangle$. Because $|\varphi_{n,\tau}\rangle$ form a basis, it is always possible to expand the state $|\psi(t)\rangle$:

$$|\psi(t)\rangle = \sum_{n,\tau} c_{n,\tau}(t)|\varphi_{n,\tau}\rangle, \quad \text{with} \quad c_{n,\tau}(t) = \langle \varphi_{n,\tau}|\psi(t)\rangle.$$

All the time dependence of $|\psi(t)\rangle$ is contained within $c_{n,\tau}(t)$. Let us project the Schrodinger equation onto each of the states $|\varphi_{n,\tau}\rangle$:

$$\begin{aligned} i\hbar \frac{d}{dt}\langle \varphi_{n,\tau}|\psi(t)\rangle &= \langle \varphi_{n,\tau}|H|\psi(t)\rangle \\ i\hbar \frac{d}{dt}c_{n,\tau}(t) &= E_n c_{n,\tau}(t). \end{aligned}$$

This equation can be integrated to give

$$c_{n,\tau}(t) = c_{n,\tau}(t_0)e^{-E_n(t-t_0)/\hbar}. \quad (2.33)$$

When H does not depend on time, to find $|\psi(t)\rangle$ given $|\psi(t_0)\rangle$, proceed as follows:

- Expand $|\psi(t_0)\rangle$ in terms of the eigenstates of H :

$$|\psi(t_0)\rangle = \sum_n \sum_\tau c_{n,\tau}(t_0) |\varphi_{n,\tau}\rangle, \quad \text{with} \quad c_{n,\tau}(t_0) = \langle \varphi_{n,\tau} | \psi(t_0) \rangle.$$

- To obtain $|\psi(t)\rangle$, multiply each coefficient $c_{n,\tau}(t_0)$ of the expansion by the term $e^{-iE_n(t-t_0)/\hbar}$:

$$|\psi(t)\rangle = \sum_n \sum_\tau c_{n,\tau}(t_0) e^{-iE_n(t-t_0)/\hbar} |\varphi_{n,\tau}\rangle. \quad (2.34)$$

or, in the continuous case,

$$|\psi(t)\rangle = \sum_\tau \int dE c_\tau(E, t_0) e^{-iE_n(t-t_0)/\hbar} |\varphi_{n,\tau}\rangle. \quad (2.35)$$

Stationary states

An important special case is that in which $|\psi(t_0)\rangle$ is itself an eigenstate of H . Then, the expansion of $|\psi(t_0)\rangle$ involves only eigenvalue of H with the same eigenvalue:

$$|\psi(t_0)\rangle = \sum_\tau c_{n,\tau}(t_0) |\varphi_{n,\tau}\rangle.$$

We notice there is no summation over n , and the passage from $|\psi(t_0)\rangle$ to $|\psi(t)\rangle$ involves only one factor of $e^{-iE_n(t-t_0)/\hbar}$, which can be taken outside the summation over τ :

$$|\psi(t)\rangle = \sum_\tau c_{n,\tau}(t_0) e^{-iE_n(t-t_0)/\hbar} |\varphi_{n,\tau}\rangle = e^{-iE_n(t-t_0)/\hbar} \sum_\tau c_{n,\tau}(t_0) |\varphi_{n,\tau}\rangle = e^{-iE_n(t-t_0)/\hbar} |\psi(t_0)\rangle.$$

$|\psi(t)\rangle$ and $|\psi(t_0)\rangle$ therefore differ only by a global phase factor. These two states are physically indistinguishable.

All the physical properties of a system which is an eigenstate of H do not vary over time: the eigenstates of H are called **stationary states**.

The state of the system will no longer evolve after the first measurement and will always remain an eigenstate of H with eigenvalue of E_k . A second measurement of the energy at any subsequent time will always yield the same result E_k as the first one.

Constants of the motion

A constant of the motion is an observable A which does not depend explicitly on time and which commutes with H :

$$\text{Constant of the motion } A \quad \frac{\partial A}{\partial t} = 0 \wedge [A, H] = 0. \quad (2.36)$$

For a conservative system, H is therefore itself a constant of the motion.

- The mean value of A does not evolve over time:

$$\frac{d}{dt}\langle A \rangle = \frac{1}{i\hbar}\langle [A, H(t)] \rangle + \langle \frac{\partial A}{\partial t} \rangle = 0.$$

- Since A and H are observables which commute, we can always find for them a system of common eigenvectors:

$$\begin{aligned} H|\varphi_{n,p,\tau}\rangle &= E_n|\varphi_{n,p,\tau}\rangle \\ A|\varphi_{n,p,\tau}\rangle &= a_p|\varphi_{n,p,\tau}\rangle \end{aligned}$$

Since the states $|\varphi_{n,p,\tau}\rangle$ are eigenstates of H , they are stationary states. But it is also an eigenstate of A .

When A is a constant of motion, there exist stationary states of the physical system ($|\varphi_{n,p,\tau}\rangle$) that always remain, for all t , eigenstates of A with the same eigenvalue a_p . The eigenvalues of A are called **good quantum numbers**.

- The probability of finding the eigenvalue a_p , when the constant of motion A is measured, is not time-dependent.

$$|\psi(t_0)\rangle = \sum_{n,p,\tau} c_{n,p,\tau}(t_0)|\varphi_{n,p,\tau}\rangle, \quad |\psi(t)\rangle = \sum_{n,p,\tau} c_{n,p,\tau}(t)|\varphi_{n,p,\tau}\rangle, \quad \text{with} \quad c_{n,p,\tau}(t) = c_{n,p,\tau}(t_0)e^{-iE_n(t-t_0)/\hbar}.$$

The probability $P(a_p, t_0)$ of finding a_p when A is measured at t_0 on the system of state $|\psi(t_0)\rangle$ is

$$P(a_p, t_0) = \sum_{n,\tau} |c_{n,p,\tau}(t_0)|^2. \quad \text{Similarly,} \quad P(a_p, t) = \sum_{n,\tau} |c_{n,p,\tau}(t)|^2.$$

We see from the coefficient relation equation that $c_{n,p,\tau}(t)$ and $c_{n,p,\tau}(t_0)$ have the same modulus. Therefore,

$$P(a_p, t) = P(a_p, t_0). \quad (2.37)$$

If all but one of the probabilities $P(a_p, t_0)$ are zero, the physical system at t_0 is in an eigenstate of A with an eigenvalue of a_k . Since the $P(a_p, t)$ do not depend on t , the state of the system at time t remains an eigenstate of A with an eigenvalue of a_k .

Bohr frequencies of a system

Let B be an arbitrary observable of the system. Its time derivative is

$$\frac{d}{dt}\langle B \rangle = \frac{1}{i\hbar}\langle [B, H] \rangle + \langle \frac{\partial B}{\partial t} \rangle.$$

For a conservative system, we know how to construct $|\psi(t)\rangle$ (2.34). Therefore, we can compute explicitly $\langle \psi(t)|B|\psi(t) \rangle$ and not only $d\langle B \rangle/dt$:

$$\begin{aligned} \langle B \rangle(t) &= \langle \psi(t)|B|\psi(t) \rangle \\ &= \left[\sum_{n',\tau'} c_{n',\tau'}^*(t_0) e^{iE_{n'}(t-t_0)/\hbar} \langle \varphi_{n',\tau'} | \right] B \left[\sum_{n,\tau} c_{n,\tau}(t_0) e^{-iE_n(t-t_0)/\hbar} | \varphi_{n,\tau} \rangle \right] \\ &= \sum_{n,\tau} \sum_{n',\tau'} c_{n',\tau'}^*(t_0) c_{n,\tau}(t_0) \langle \varphi_{n',\tau'} | B | \varphi_{n,\tau} \rangle e^{i(E_{n'} - E_n)(t-t_0)/\hbar}. \end{aligned}$$

If we assume B does not depend explicitly on time, the matrix elements $\langle \varphi_{n',\tau'} | B | \varphi_{n,\tau} \rangle$ are constant. The evolution of $\langle B \rangle(t)$ is described by a series of oscillating terms, whose frequencies

$$\text{Bohr frequencies of the system} \quad \nu_{n',n} = \frac{1}{2\pi} \frac{|E_{n'} - E_n|}{\hbar} = \left| \frac{E_{n'} - E_n}{h} \right|$$

are characteristic of the system under consideration, but independent of B and the initial state of the system. The importance of each frequency $\nu_{n',n}$ depends on the matrix elements $\langle \varphi_{n',\tau'} | B | \varphi_{n,\tau} \rangle$. This is the origin of the selection rules which indicate what frequencies can be emitted or absorbed under given conditions. One would have to study the non-diagonal matrix elements $n \neq n'$ of the various atomic operator such as the electric and magnetic dipoles, etc.

Using the $\langle B \rangle(t)$ expression, we can say that the mean value of a constant of the motion is always time-independent. The only terms of $\langle B \rangle$ that are non-zero are thus constant.

Time-energy uncertainty relation

2.5 The superposition principle and physical predictions

One of the important consequences of the first postulate, when it is combined with the others, is the appearance of **interference effects**.

2.6 Evolution operator

The transformation of $|\psi(t_0)\rangle$ into $|\psi(t)\rangle$ is linear. Therefore, there exists a linear operator $U(t, t_0)$ such that

$$\text{Evolution operator} \quad |\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle, \quad (2.38)$$

where $U(t, t_0)$ is the **evolution operator** of the system.

2.6.1 General properties

From (2.38) we know that

$$U(t_0, t_0) = \mathbb{1}. \quad (2.39)$$

If we substitute the linear operator into the Schrödinger equation, we obtain:

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) |\psi(t_0)\rangle = H(t) U(t, t_0) |\psi(t_0)\rangle \implies i\hbar \frac{\partial}{\partial t} U(t, t_0) = H(t) U(t, t_0). \quad (2.40)$$

This is a first-order differential equation completely defined $U(t, t_0)$. Equations (2.39) and (2.40) can be condensed into a single integral form:

$$U(t, t_0) = \mathbb{1} = \int_{t_0}^t H(t') U(t', t_0) dt. \quad (2.41)$$

Let's now take three instants t'', t', t so that $t'' < t' < t$, then

$$\left. \begin{aligned} |\psi(t)\rangle &= U(t, t') |\psi(t')\rangle \\ |\psi(t')\rangle &= U(t', t'') |\psi(t'')\rangle \end{aligned} \right\} \implies |\psi(t)\rangle = U(t, t') U(t', t'') |\psi(t'')\rangle = U(t, t'') |\psi(t'')\rangle.$$

From last expression, we have:

$$U(t, t')U(t', t'') = U(t, t'') \quad (2.42)$$

If we set $t = t''$ and interchange the roles of t and t' we have

$$\mathbb{1} = U(t', t)U(t, t') \implies U(t', t) = U^{-1}(t, t'). \quad (2.43)$$

On the other hand, the evolution operator between two instants separated by dt is :

$$d|\psi(t)\rangle = |\psi(t + dt)\rangle - |\psi(t)\rangle = -\frac{i}{\hbar}H(t)|\psi(t)\rangle dt.$$

From this we have

$$|\psi(t + dt)\rangle = \left[\mathbb{1} - \frac{i}{\hbar}H(t) dt \right] |\psi(t)\rangle = U(t + dt, t)|\psi(t)\rangle.$$

That is, we have the **infinitesimal evolution operator**:

$$\text{Infinitesimal evolution operator} \quad U(t + dt, t) = \mathbb{1} - \frac{i}{\hbar}H(t) dt. \quad (2.44)$$

Since $H(t)$ is Hermitian, $U(t + dt, t)$ is unitary. It is not surprising that the evolution operator conserves the norm of vectors on which it acts. We saw previously that the norm of the state vector does not change over time.

2.6.2 Case of conservative systems

When the operator H does not depend on time, equation (2.40) can be integrated easily:

$$U(t, t_0) = e^{-iH(t-t_0)/\hbar}. \quad (2.45)$$

Applying this operator on a state vector $|\varphi_{n,\tau}\rangle$ yields:

$$U(t, t_0)|\varphi_{n,\tau}\rangle = e^{-iH(t-t_0)/\hbar}|\varphi_{n,\tau}\rangle = e^{-iE_n(t-t_0)/\hbar}|\varphi_{n,\tau}\rangle. \quad (2.46)$$

2.7 Infinite potential well

Formula sheet

2.7.1 Useful formulas

| | | | |
|--|---|---|---|
| Closure relation (discrete) | $\sum_k \sum_{i=1}^{g_k} v_k^i\rangle \langle v_k^i = \mathbb{1}$ | Closure relation (continuous) | $\int_{\beta} d\beta \omega_{\beta}\rangle \langle \omega_{\beta} = \mathbb{1}$ |
| Glauber Formula | $e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}$ | Generalized uncertainty relation | $\Delta A \Delta B \geq \frac{1}{2} \langle [A, B] \rangle $ |
| Function of an operator | $F(A) = \sum_{n=0}^{\infty} f_n (A - a)^n$ | | $\Delta Q = \sqrt{\langle Q^2 \rangle - \langle Q \rangle^2}$ |
| Eigenequation of $F(A)$ | $F(A) \psi\rangle = F(\lambda) \psi\rangle$ | | |
| Transformation $\{u\} \rightarrow \{v\}$ | $\mathbb{M}_{jk} = \langle u_j v_k \rangle$ | $ \psi\rangle_{\{u\}} = \mathbb{M} \psi\rangle_{\{v\}}$ $A_{\{u\}} = \mathbb{M} A_{\{v\}} \mathbb{M}^{\dagger}$ | $ \psi\rangle_{\{v\}} = \mathbb{M}^{\dagger} \psi\rangle_{\{u\}}$ $A_{\{v\}} = \mathbb{M}^{\dagger} A_{\{u\}} \mathbb{M}$ |

2.7.2 Basis

| Quantity | Discrete basis (sum over j, k) | Continuous basis (integrate over β, β') |
|---|---|--|
| $\mathbb{1}$ | $= \sum v_k\rangle \langle v_k $ | $= \int d\beta \omega_{\beta}\rangle \langle \omega_{\beta} $ |
| $ \psi\rangle = \mathbb{1} \psi\rangle$ | $= \sum v_k\rangle \langle v_k \psi\rangle$ | $= \int d\beta \omega_{\beta}\rangle \langle \omega_{\beta} \psi\rangle$ |
| $\langle \varphi = \langle \varphi \mathbb{1}$ | $= \sum \langle \varphi v_k\rangle \langle v_k $ | $= \int d\beta \langle \varphi \omega_{\beta}\rangle \langle \omega_{\beta} $ |
| $A = \mathbb{1}A\mathbb{1}$ | $= \sum \sum v_j\rangle \langle v_j A v_k\rangle \langle v_k $ | $= \iint d\beta d\beta' \omega_{\beta}\rangle \langle \omega_{\beta} A \omega_{\beta'}\rangle \langle \omega_{\beta'} $ |

| Quantity | X representation | P_x representation |
|----------------|---|--|
| \hat{X} | x | $i\hbar \partial/\partial p$ |
| P_x | $-i\hbar \partial/\partial x$ | p |
| $ x'\rangle$ | $\langle x x'\rangle = \delta(x - x')$ | $\langle p x'\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(-ix'p/\hbar)$ |
| $ p'\rangle$ | $\langle x p'\rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp(ixp'/\hbar)$ | $\langle p p'\rangle = \delta(p - p')$ |
| $ \psi\rangle$ | $\langle x \psi\rangle = \psi(x)$ | $\langle p \psi\rangle = \tilde{\psi}(p)$ |

Fourier transforms for 3D wavefunctions

| | |
|--|--|
| $\tilde{\psi}(\mathbf{p}) = \mathcal{F}[\psi(\mathbf{r})] = \left(\frac{1}{2\pi\hbar}\right)^{3/2} \int_{-\infty}^{\infty} d^3\mathbf{r} e^{-i\mathbf{r}\cdot\mathbf{p}/\hbar} \psi(\mathbf{r})$ | $\psi(\mathbf{r}) = \mathcal{F}^{-1}[\tilde{\psi}(\mathbf{p})] = \left(\frac{1}{2\pi\hbar}\right)^{3/2} \int_{-\infty}^{\infty} d^3\mathbf{p} e^{i\mathbf{r}\cdot\mathbf{p}/\hbar} \tilde{\psi}(\mathbf{p})$ |
| $\mathcal{F}[\psi^{(n)}(x)] = \left(\frac{ip}{\hbar}\right)^n \tilde{\psi}(p)$ | $\tilde{\psi}^{(n)}(p) = \mathcal{F}\left[\left(-\frac{ix}{\hbar}\right)^n \psi(x)\right]$ |
| $\tilde{\psi}(p - p_0) = \mathcal{F}[e^{ip_0x/\hbar} \psi(x)]$ | $e^{-ipx_0/\hbar} \tilde{\psi}(p) = \mathcal{F}[\psi(x - x_0)]$ |
| $\mathcal{F}[\psi(cx)] = \tilde{\psi}(p/c)/ c $ | $\int_{-\infty}^{\infty} dx \varphi^*(x) \psi(x) = \int_{-\infty}^{\infty} dp \tilde{\varphi}^*(p) \tilde{\psi}(p)$ |
| $\psi(x) \text{ real } [\tilde{\psi}(p)]^* = \tilde{\psi}(-p)$ | $\psi(x) \text{ imaginary } [\tilde{\psi}(p)]^* = -\tilde{\psi}(-p)$ |
| $\Delta x \Delta p \geq \hbar$ | |

Commutators

Key points

- When a matrix has a block form, we can compute the eigenvalues in each submatrix.
- The orthonormalized eigenvectors of a matrix create the basis by concatenating them.
- If the matrix is diagonal, the exponential acts directly onto the elements.

$$\begin{array}{l|l}
[A, B] = -[B, A] & [A + B, C + D] = [A, C] + [A, D] + [B, C] + [B, D] \\
[A, B]^\dagger = [B^\dagger, A^\dagger] & [A, BC] = [A, B]C + B[A, C] \\
[F(A), A] = 0 & [A, B] = 0 \implies [F(A), B] = [A, F(B)] = [F(A), F(B)] = 0 \\
[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0 & [A, [A, B]] = [B, [A, B]] = 0 \implies [A, F(B)] = [A, B] \frac{dF(B)}{dB} \\
e^A e^B = e^{A+B} e^{\frac{1}{2}[A, B]} \quad ([A, [A, B]] = [B, [A, B]] = 0) & [A, [A, B]] = [B, [A, B]] = 0 \implies [F(A), B] = [A, B] \frac{dF(A)}{dA} \\
[X, P] = i\hbar & [H, X] = -\frac{i\hbar}{m} P \\
[H, P] = i\hbar \frac{dV(X)}{dX} & \langle \varphi_n | [A, H] | \varphi_n \rangle = 0, \quad \forall A
\end{array}$$

- Evolution operator is defined as $U = e^{-iHt/\hbar}$, and then it evolves the state by matrix multiplication $U|\psi\rangle$.
- Eigenvectors that are related in the eigenequation must be considered to the construction of the new basis.
- You can reduce the dimension of an operator to its eigensubspace when only acting inside it.
- To know the action of an operator you can stimulate it by applying $|\phi\rangle$ or $\langle\psi|$.

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