Notes of Quantum Mechanics

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Preface

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Chapter 1

Mathematical Formalism

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 proabailities of measurements.

State

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

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

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

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 $\psi(\boldsymbol{r}, t)$ which are everywhere defined, continuous, and infinitely differenciable 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 caleld scalars.

$$\begin{array}{l|l}
\text{Commutativity of vector addition} & \boldsymbol{u} + \boldsymbol{v} = \boldsymbol{v} + \boldsymbol{u} \\
\text{Associativity of vector addition} & (\boldsymbol{u} + \boldsymbol{v}) + \boldsymbol{w} = \boldsymbol{u} + (\boldsymbol{v} + \boldsymbol{w}) \\
\text{Identity element of vector addition} & \exists \boldsymbol{0}, \boldsymbol{v} \in V : \quad \boldsymbol{v} + \boldsymbol{0} = \boldsymbol{v} \\
\text{Inverse element of vector addition} & \forall \boldsymbol{v} \in V, \; \exists -\boldsymbol{v} \in V : \quad \boldsymbol{v} + (-\boldsymbol{v}) = \boldsymbol{0} \\
\text{Associativity of scalar multiplication} & \alpha(\beta \boldsymbol{v}) = (\alpha\beta)\boldsymbol{v} \\
\text{Distributivity over vector addition} & \alpha(\boldsymbol{u} + \boldsymbol{v}) = \alpha\boldsymbol{u} + \alpha\boldsymbol{v} \\
\text{Distributivity over scalar addition} & (\alpha + \beta)\boldsymbol{v} = \alpha\boldsymbol{v} + \beta\boldsymbol{v} \\
\text{Identity element of scalar multiplication} & \boldsymbol{1}\boldsymbol{v} = \boldsymbol{v}
\end{array} \tag{1.2}$$

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 $\mathscr{F}$

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

1.1.1 Scalar product

With each pair of orderer elements of $\mathscr{F}$, $(\varphi(\boldsymbol{r}), \psi(\boldsymbol{r}))$, we associate a *complex number*:

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

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

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

We also have the Schwarz inequality defined with the norms:

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

1.1.2 Linear operators

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

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

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 $\varphi(\boldsymbol{r}) = B\psi(\boldsymbol{r})$:

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

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

$$\boxed{[A, B] = AB - BA}\,. \tag{1.8}$$

1.1.3 Discrete orthonormal bases in $\mathscr{F}$: $\{u_i(\boldsymbol{r})\}$

Definition of discrete orthonormal bases

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

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

$$\text{Orthonormalization relation} \qquad \boxed{(u_i, u_j) = \int d^3r \; u_i^*(\boldsymbol{r}) u_j(\boldsymbol{r}) = \delta_{ij}}\,, \tag{1.9}$$

  where δ_{ij} is the kronecker function:

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

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

$$\text{Expansion} \qquad \boxed{\psi(\boldsymbol{r}) = \sum_i c_i u_i(\boldsymbol{r})}\,, \tag{1.11}$$

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

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

Thus,

$$\text{Coefficient expansion} \qquad \boxed{c_i = (u_i, \psi) = \int d^3r \; u_i^*(\boldsymbol{r})\psi(\boldsymbol{r})}\,. \tag{1.12}$$

Once projected in $\{u_i(\boldsymbol{r})\}$ it is equivalent to specify $\psi(\boldsymbol{r})$ or the set of c_i, which represent $\psi(\boldsymbol{r})$ in the $\{u_i(\boldsymbol{r})\}$ 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 $\varphi(\boldsymbol{r}), \psi(\boldsymbol{r})$,

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

Therefore, the scalar product is:

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

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

Closure relation

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

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

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

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

$$\text{Closure relation} \qquad \boxed{\sum_i u_i(\boldsymbol{r}) u_i^*(\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')}\,. \tag{1.15}$$

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

1.1.4 Bases not belonging to $\mathscr{F}$

The $\{u_i(\boldsymbol{r})\}$ bases are composed of square-integrable functions. It can also be convenient to introduce bases of functions **not belonging** to $\mathscr{F}$ or L_2, but in terms of which any wavefunction $\psi(\boldsymbol{r})$ 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 $p/\hbar$

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

The integral of $|v_p(x)|^2 = \frac{1}{2\pi\hbar}$ over $x \in \mathbb{R}$ diverges, therefore $v_p(x) \notin \mathscr{F}_x$. 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:

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

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

The two formulas can be compared to equations (1.11) and (1.12). In this case, every function $\psi(x) \in \mathscr{F}_x$ 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:

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

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

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

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,

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

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

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

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

$$\text{Expansion} \qquad \psi(\boldsymbol{r}) = \int d^3p\ \bar{\psi}(\boldsymbol{p}) v_{\boldsymbol{p}}(\boldsymbol{r}) \tag{1.23}$$

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

$$\text{scalar product} \qquad (\varphi, \psi) = \int d^3p\ \bar{\varphi}^*(\boldsymbol{p}) \bar{\psi}(\boldsymbol{p}) \tag{1.25}$$

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

$$\text{Orthornormalization relation} \qquad (v_{\boldsymbol{p}}, v_{\boldsymbol{p}'}) = \delta(\boldsymbol{p} - \boldsymbol{p}') \tag{1.27}$$

The $v_p(\boldsymbol{r})$ can be considered to constitute a **continuous** basis.

Delta function

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

$$\xi_{\boldsymbol{r}_0}(\boldsymbol{r}) = \delta(\boldsymbol{r} - \boldsymbol{r}_0). \tag{1.28}$$

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

Then, we can have the following

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

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

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

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

We also list, the other formulas:

$$\text{scalar product} \qquad (\varphi, \psi) = \int d^3r_0\ \varphi^*(\boldsymbol{r}_0)\psi(\boldsymbol{r}_0) \tag{1.31}$$

$$\text{Closure relation} \qquad \int d^3r_0\ \xi_{\boldsymbol{r}_0}(\boldsymbol{r})\xi^*_{\boldsymbol{r}_0}(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}') \tag{1.32}$$

$$\text{Orthonormalization relation} \qquad (\xi_{\boldsymbol{r}_0}, \xi_{\boldsymbol{r}'_0}) = \delta(\boldsymbol{r}_0 - \boldsymbol{r}'_0) \tag{1.33}$$

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

A physical state must **always** correspond to a qaure-integrable wavefunction. In no case $v_p(\boldsymbol{r})$ and $\xi_{\boldsymbol{r}_0}(\boldsymbol{r})$ 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 $\boldsymbol{r}$, $\{w_\alpha(\boldsymbol{r})\}$, labeled by a continuous index α, which satisfy the closure and orthonormalization relations:

$$\text{Orthonormalization relation} \qquad (w_\alpha, w_{\alpha'}) = \int d^3r\ w^*_\alpha(\boldsymbol{r})w_{\alpha'}(\boldsymbol{r}) = \delta(\alpha-\alpha') \tag{1.34}$$

$$\text{Closure relation} \qquad \int d\alpha\ w_\alpha(\boldsymbol{r})w^*_\alpha(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{1.35}$$

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

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

$$\text{Orthonormalization relation for mixed basis} \qquad \begin{array}{l} (u_i, u_j) = \delta_{ij} \\ (w_\alpha, w_{\alpha'}) = \delta(\alpha-\alpha') \\ (u_i, w_\alpha) = 0 \end{array}. \tag{1.36}$$

And the closure relation becomes:

$$\text{Closure relation for mixed basis} \qquad \sum_i u_i(\boldsymbol{r})u^*_i(\boldsymbol{r}') + \int d\alpha\ w_\alpha(\boldsymbol{r})w^*_\alpha(\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}'). \tag{1.37}$$

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

$$\text{Expansion} \qquad \psi(\boldsymbol{r}) = \int d\alpha\ c(\alpha)w_\alpha(\boldsymbol{r}) \tag{1.38}$$

$$\text{Coefficient expansion} \qquad c(\alpha) = (w_\alpha, \psi) = \int d^3r'\ w^*_\alpha(\boldsymbol{r}')\psi(\boldsymbol{r}') \tag{1.39}$$

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

The squared norm of the wavefunction with itself is then

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

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:

$$\text{Transformation } \{u_i(\boldsymbol{r})\} \longleftrightarrow \{w_\alpha(\boldsymbol{r})\} \qquad \boxed{\begin{aligned} & i \longleftrightarrow \alpha \\ & \sum_i \longleftrightarrow \int d\alpha \\ & \delta_{ij} \longleftrightarrow \delta(\alpha - \alpha') \end{aligned}} \tag{1.42}$$

Table 1.1 Fundamental formulas for discrete and continuous basis.

Property	Discrete basis $\{u_i(\boldsymbol{r})\}$	Continuous basis $\{w_\alpha(\boldsymbol{r})\}$
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	$\sum_i u_i(\boldsymbol{r}) u_i^*(\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')$	$\int d\alpha\, w_\alpha(\boldsymbol{r}) w_\alpha^*(\boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')$
Expansion	$\psi(\boldsymbol{r}) = \sum_i c_i u_i(\boldsymbol{r})$	$\psi(\boldsymbol{r}) = \int d\alpha\, c(\alpha) w_\alpha(\boldsymbol{r})$
Components	$c_i = (u_i, \psi)$	$c(\alpha) = (w_\alpha, \psi)$

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