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 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:

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

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*:

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

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**:

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

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:

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

  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:

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

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:

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

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

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

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:

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

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

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:

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

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

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

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	$(\psi, \psi) = \sum_i \lvert c_i\rvert^2$	$(\psi, \psi) = \int d\alpha\, \lvert c(\alpha)\rvert^2$
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	$c_i = (u_i, \psi)$	$c(\alpha) = (w_\alpha, \psi)$

1.2 Dirac notation

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

1.2.2 Linear operators

1.2.3 Hermitian conjugation (adjoint)

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