

# **Notes of Quantum Mechanics**

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# Preface

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# Contents

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<b>Preface</b>	<b>2</b>
<b>1 Postulates of Quantum Mechanics</b>	<b>8</b>
1.1 Introduction . . . . .	9
1.2 Statements of the postulates . . . . .	9
1.3 The physical interpretation of the postulates . . . . .	13
1.4 Physical implications of the Schrodinger equation . . . . .	16
1.5 The superposition principle and physical predictions . . . . .	21
1.6 Evolution operator . . . . .	21
1.7 One-dimensional Gaussian wave packet (G1) . . . . .	22
1.8 Particle in an infinite potential well . . . . .	22
1.9 Shrodinger and Heisenberg pictures . . . . .	24
1.10 The density operator . . . . .	25

# List of Figures

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# List of Tables

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# Listings

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## Chapter 1

# Postulates of Quantum Mechanics

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1.1	Introduction . . . . .	9
1.2	Statements of the postulates . . . . .	9
1.3	The physical interpretation of the postulates . . . . .	13
1.4	Physical implications of the Schrodinger equation . . . . .	16
1.5	The superposition principle and physical predictions . . . . .	21
1.6	Evolution operator . . . . .	21
1.7	One-dimensional Gaussian wave packet (G1) . . . . .	22
1.8	Particle in an infinite potential well . . . . .	22
1.9	Schrodinger and Heisenberg pictures . . . . .	24
1.10	The density operator . . . . .	25

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## 1.1 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.

## 1.2 Statements of the postulates

### 1.2.1 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**.

### 1.2.2 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  $\{|u_n^i\rangle\}$ :

$$A|u_n^i\rangle = a_n|u_n^i\rangle, \quad i = 1, 2, \dots, g_n \implies |\psi\rangle = \sum_n \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle. \quad (1.1)$$

The probability now becomes

$$P(a_n) = \sum_{i=1}^{g_n} |c_n^i|^2 = \sum_{i=1}^{g_n} |\langle u_n^i|\psi\rangle|^2. \quad (1.2)$$

### 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  $\psi$  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  $\alpha$  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  $\alpha_1$  and  $\alpha_2$  is the continuous projection of  $\psi$  onto that interval:

$$P(\alpha_1 < \alpha < \alpha_2) = \langle \psi | P_{\alpha_1, \alpha_2} | \psi \rangle = \int_{\alpha_1}^{\alpha_2} |\langle v_\alpha | \psi \rangle|^2 d\alpha, \quad P_{\alpha_1, \alpha_2} = \int_{\alpha_1}^{\alpha_2} |v_\alpha\rangle \langle v_\alpha| d\alpha. \quad (1.3)$$

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

$$\begin{array}{ll} \text{Discrete case} & \text{Continuous case} \\ P(a_n) = \frac{1}{\langle \psi | \psi \rangle} \sum_{i=1}^{g_n} |c_n^i|^2 & \rho(\alpha) = \frac{1}{\langle \psi | \psi \rangle} |c(\alpha)|^2. \end{array} \quad (1.4)$$

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.

### 1.2.3 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  $a_n$ :

$$\text{State of collapse} \quad |\psi\rangle \xrightarrow{(a_n)} |u_n\rangle. \quad (1.5)$$

- 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 (1.1)):

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

And the state of collapse just after the measurement is

$$\text{State of collapse} \quad |\psi\rangle \xrightarrow{(a_n)} \frac{1}{\sqrt{\sum_{i=1}^{g_n} |c_n^i|^2}} \sum_{i=1}^{g_n} c_n^i |u_n^i\rangle. \quad (1.6)$$

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  $a_n$ :

$$|\psi\rangle \xrightarrow{(a_n)} \frac{P_n |\psi\rangle}{\sqrt{\langle \psi | P_n | \psi \rangle}} \quad (1.7)$$

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

### 1.2.4 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:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle, \quad (1.8)$$

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

### 1.2.5 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.

## 1.3 The physical interpretation of the postulates

### 1.3.1 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 (1.4)):

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

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

$$\langle x|p\rangle = (2\pi\hbar)^{-1/2} e^{\frac{ipx}{\hbar}}. \quad (1.9)$$

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:

$$dP(p) = |\langle p|\psi\rangle|^2 dp = |\tilde{\psi}(p)|^2 dp. \quad (1.10)$$

### 1.3.2 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.

### 1.3.3 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

$$\langle A \rangle_\psi = \langle \psi|A|\psi\rangle \quad (1.11)$$

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

$$\lim_{N \rightarrow \infty} \frac{N(a_n)}{N} = P(a_n), \quad \text{and} \quad \sum_n N(a_n) = N. \quad (1.12)$$

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

$$\langle A \rangle_\psi = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_n a_n N(a_n) = \sum_n a_n P(a_n). \quad (1.13)$$

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:

$$\lim_{N \rightarrow \infty} \frac{dN(\alpha)}{N} = dP(\alpha). \quad (1.14)$$

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

$$\langle A \rangle_\psi = \lim_{N \rightarrow \infty} \frac{1}{N} \int \alpha dN(\alpha) = \int \alpha dP(\alpha). \quad (1.15)$$

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

$$\text{Mean value of } A \quad \langle A \rangle_\psi = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle}. \quad (1.16)$$

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

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

### 1.3.4 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**  $\Delta A$  as

$$\text{RMS deviation} \quad \Delta A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle} = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}. \quad (1.17)$$

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

$$\begin{aligned} \Delta X \cdot \Delta P_x &\geq \frac{\hbar}{2} \\ \Delta Y \cdot \Delta P_y &\geq \frac{\hbar}{2} \\ \Delta Z \cdot \Delta P_z &\geq \frac{\hbar}{2} \end{aligned} \quad \text{Heisenberg relations} \quad (1.18)$$

### 1.3.5 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

$$P(a_n) = \sum_{p,i} |c_{n,p,i}|^2. \quad (1.19)$$

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

$$P_{a_n}(b_p) = \frac{1}{\sum_{p,i} |c_{n,p,i}|^2} \sum_i |c_{n,p,i}|^2. \quad (1.20)$$

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,

$$P(a_n, b_p) = P(a_n)P_{a_n}(b_p) = \sum_i |c_{n,p,i}|^2. \quad (1.21)$$

The state of the system becomes immediately after the second measurement

$$|\psi''_{n,p}\rangle = \frac{1}{\sqrt{\sum_i |c_{n,p,i}|^2}} \sum_i c_{n,p,i} |a_n, b_p, i\rangle. \quad (1.22)$$

$|\psi''_{n,p}\rangle$  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

$$P(b_p, a_n) = \sum_i |c_{n,p,i}|^2, \quad \text{and} \quad |\psi''_{p,n}\rangle = \frac{1}{\sqrt{\sum_i |c_{n,p,i}|^2}} \sum_i c_{n,p,i} |a_n, b_p, i\rangle. \quad (1.23)$$

### 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:

$$P(a_n, b_p) = P(b_p, a_n) = \sum_i |c_{n,p,i}|^2 = \sum_i |\langle a_n, b_p, i | \psi \rangle|^2, \quad \text{and} \quad (1.24)$$

$$|\psi''_{n,p}\rangle = |\psi''_{p,n}\rangle = \frac{1}{\sqrt{\sum_i |c_{n,p,i}|^2}} \sum_i c_{n,p,i} |a_n, b_p, i\rangle. \quad (1.25)$$

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

## 1.4 Physical implications of the Schrodinger equation

Recall the Schrodinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi\rangle. \quad (1.26)$$

### 1.4.1 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 (1.26) is linear and homogeneous, then their slutions are linearly superposable:

$$|\psi(t_0)\rangle = \lambda_1|\psi_1(t_0)\rangle + \lambda_2|\psi_2(t_0)\rangle \implies |\psi(t)\rangle = \lambda_1|\psi_1(t)\rangle + \lambda_2|\psi_2(t)\rangle. \quad (1.27)$$

### 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

$$\langle\psi(t)|\psi(t)\rangle = \int d^3r |\psi(\mathbf{r}, t)|^2 = \langle\psi(t_0)|\psi(t_0)\rangle = 1. \quad (1.28)$$

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

$$\langle A \rangle(t) = \langle\psi(t)|A|\psi(t)\rangle. \quad (1.29)$$

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,

$$\text{Evolution of the mean value of } A \quad \frac{d}{dt}\langle A \rangle = \frac{1}{i\hbar}\langle[A, H(t)]\rangle + \left\langle \frac{\partial A}{\partial t} \right\rangle. \quad (1.30)$$

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 (1.30) 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**:

$$\text{Ehrenfest's theorem} \quad \begin{aligned} \frac{d}{dt}\langle \mathbf{R} \rangle &= \frac{1}{m}\langle \mathbf{P} \rangle \\ \frac{d}{dt}\langle \mathbf{P} \rangle &= -\langle \nabla V(\mathbf{R}) \rangle \end{aligned} \quad (1.31)$$

classical limits of the Ehrenfest's theorem

### 1.4.2 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):

$$H|\varphi_{n,\tau}\rangle = E_n|\varphi_{n,\tau}\rangle. \quad (1.32)$$

$\tau$  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

$$c_{n,\tau}(t) = c_{n,\tau}(t_0) e^{-E_n(t-t_0)/\hbar}. \quad (1.33)$$

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  $e^{-iE_n(t-t_0)/\hbar}$ :

$$|\psi(t)\rangle = \sum_n \sum_\tau c_{n,\tau}(t_0) e^{-iE_n(t-t_0)/\hbar} |\varphi_{n,\tau}\rangle. \quad (1.34)$$

or, in the continuous case,

$$|\psi(t)\rangle = \sum_\tau \int dE c_\tau(E, t_0) e^{-iE_n(t-t_0)/\hbar} |\varphi_{n,\tau}\rangle. \quad (1.35)$$

### 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  $\tau$ :

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

$|\psi(t)\rangle$  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  $H$ :

$$\text{Constant of the motion } A \quad \frac{\partial A}{\partial t} = 0 \wedge [A, H] = 0. \quad (1.36)$$

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

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

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

- 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,

$$P(a_p, t) = P(a_p, t_0). \quad (1.37)$$

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

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

For a conservative system, we know how to construct  $|\psi(t)\rangle$  (1.34). 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

## 1.5 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**.

## 1.6 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

$$\text{Evolution operator} \quad |\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle, \quad (1.38)$$

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

### 1.6.1 General properties

From (1.38) we know that

$$U(t_0, t_0) = \mathbb{1}. \quad (1.39)$$

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

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) |\psi(t_0)\rangle = H(t) U(t, t_0) |\psi(t_0)\rangle \implies i\hbar \frac{\partial}{\partial t} U(t, t_0) = H(t) U(t, t_0). \quad (1.40)$$

This is a first-order differential equation completely defined  $U(t, t_0)$ . Equations (1.39) and (1.40) can be condensed into a single integral form:

$$U(t, t_0) = \mathbb{1} = \int_{t_0}^t H(t') U(t', t_0) dt. \quad (1.41)$$

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:

$$U(t, t')U(t', t'') = U(t, t'') \quad (1.42)$$

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

$$\mathbb{1} = U(t', t)U(t, t') \implies U(t', t) = U^{-1}(t, t'). \quad (1.43)$$

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**:

$$\text{Infinitesimal evolution operator} \quad U(t + dt, t) = \mathbb{1} - \frac{i}{\hbar}H(t) dt. \quad (1.44)$$

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.

### 1.6.2 Case of conservative systems

When the operator  $H$  does not depend on time, equation (1.40) can be integrated easily:

$$U(t, t_0) = e^{-iH(t-t_0)/\hbar}. \quad (1.45)$$

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

$$U(t, t_0)|\varphi_{n,\tau}\rangle = e^{-iH(t-t_0)/\hbar}|\varphi_{n,\tau}\rangle = e^{-iE_n(t-t_0)/\hbar}|\varphi_{n,\tau}\rangle. \quad (1.46)$$

## 1.7 One-dimensional Gaussian wave packet (G1)

## 1.8 Particle in an infinite potential well

### 1.8.1 Introduction (H1)

### 1.8.2 Distribution of the momentum values in a stationary state

We have seen that the stationary states of the particle correspond to the energies

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad (1.47)$$

and to the wave functions

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, \quad (1.48)$$

where  $a$  is the width of the well.

The probability of a measurement of the momentum  $P$  of the particle yielding a result between  $p$  and  $p + dp$  is

$$\bar{P}_n(p) dp = |\bar{\varphi}_n(p)|^2 dp, \quad \text{with} \quad (1.49)$$

$$\begin{aligned} \bar{\varphi}_n(p) &= \frac{1}{\sqrt{2\pi\hbar}} \int_0^a \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} e^{-ipx/\hbar} dx \\ &= \frac{1}{2i\sqrt{n\hbar a}} \int_0^a \left[ e^{i(\frac{n\pi}{a} - \frac{p}{\hbar})x} - e^{-i(\frac{n\pi}{a} + \frac{p}{\hbar})x} \right] dx \\ &= \frac{1}{2i} \sqrt{\frac{a}{\pi\hbar}} e^{i(\frac{n\pi}{a} - \frac{pa}{2\hbar})} \left[ F\left(p - \frac{n\pi\hbar}{a}\right) + (-1)^{n+1} F\left(p + \frac{n\pi\hbar}{a}\right) \right], \quad \text{with} \quad F(p) = \frac{\sin(pa/2\hbar)}{pa/2\hbar}. \end{aligned} \quad (1.50)$$

The function inside the brackets in equation (1.50) is even if  $n$  is odd, and odd if  $n$  is even. The probability density  $\bar{P}_n(p)$  is therefore an even function of  $p$  in all cases, so that

$$\text{Mean value of the momentum in the energy state } E_n \quad \langle P \rangle_n = \int_{-\infty}^{\infty} \bar{P}_n(p) p dp = 0. \quad (1.51)$$

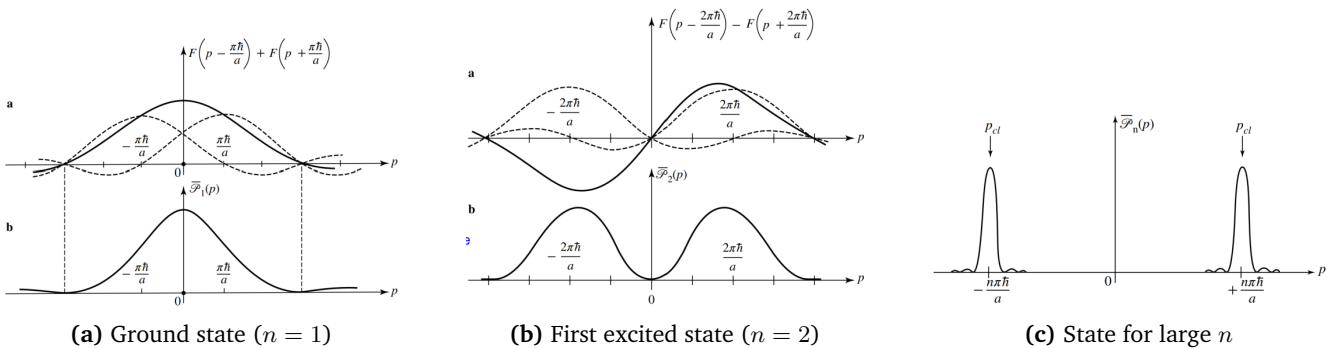
In the same way, we can compute  $\langle P^2 \rangle_n$ . Using the fact that in the  $\{|x\rangle\}$  representation  $P$  acts like  $-i\hbar\partial_x$  and performing an integration by parts, we obtain:

$$\langle P^2 \rangle_n = \hbar^2 \int_0^a \left| \frac{d\varphi_n}{dx} \right|^2 dx = \hbar^2 \int_0^a \frac{2}{a} \left( \frac{n\pi}{a} \right)^2 \cos^2 \frac{n\pi x}{a} dx = \left( \frac{n\pi\hbar}{a} \right)^2. \quad (1.52)$$

Using both  $\langle P \rangle_n$  and  $\langle P^2 \rangle_n$  we get:

$$\Delta P_n = \sqrt{\langle P^2 \rangle_n - \langle P \rangle_n^2} = \frac{n\pi\hbar}{a}.$$

We can plot the probability density  $\bar{P}_n(p)$  for different values of  $n \in \{1, 2, \text{large}\}$ . The results are illustrated in the following plot. We can see that as  $n$  increases, the interference term between  $F(p - n\pi\hbar/a)$



and  $F(p + n\pi\hbar/a)$  is negligible:

$$\bar{P}_n(p) = \frac{a}{4\pi\hbar} \left[ F\left(p - \frac{n\pi\hbar}{a}\right) + (-1)^{n+1} F\left(p + \frac{n\pi\hbar}{a}\right) \right]^2 \approx \frac{a}{4\pi\hbar} \left[ F^2\left(p - \frac{n\pi\hbar}{a}\right) + F^2\left(p + \frac{n\pi\hbar}{a}\right) \right].$$

In this limit, it is then possible to predict with almost complete certainty the results of a measurement of the momentum of the particle in the state  $|\varphi_n\rangle$ : the value will be nearly equal to  $\pm \frac{n\pi\hbar}{a}$ , with accuracy increasing as  $n$  grows.

- The momentum of a classical particle of energy  $E_n$  is:

$$\frac{p_{cl}^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \longrightarrow p_{cl} = \pm \frac{n\pi\hbar}{a}.$$

When  $n$  is large, the two peaks of  $\bar{P}_n(p)$  therefore correspond to the classical values of the momentum.

- For large  $n$ , although the absolute value of the momentum is well-defined, its sign is not. This is why  $\Delta P_n$  is large: the rms deviation reflects the distance between the two peaks, it is no longer related to their widths.

### 1.8.3 Evolution of the particle's wave function

### 1.8.4 Perturbation created by a position measurement

## 1.9 Shcrodinger and Heisenberg pictures

The evolution of the system is entirely contained in that of the state vector  $|\psi(t)\rangle$  (written here  $|\psi_S(t)\rangle$ ), and is obtained from the Schrodinger equation. This is why this approach is called *Schrodinger picture*.

We know that all the predictions of quantum mechanics are expressed in terms of scalar products of a bra and a ket or matrix elements of operators. These quantities are invariant when the same unitary transformation is performed on the kets and on the operators. This transformation can be chosen so as to make the transform of a ket  $|\psi_S(t)\rangle$  a time-independent ket. The transforms of the observable above then depend on time. We thus obtain the *Heisenberg picture*.

We will assign the subscript  $S$  for Schrodinger and  $H$  for Heisenberg pictures.

The state vector  $|\psi_S(t)\rangle$  at  $t$  is expressed in terms of  $|\psi_S(t_0)\rangle$  by the relation:

$$|\psi_S(t)\rangle = U(t, t_0)|\psi_S(t_0)\rangle.$$

Since this operator is unitary, it is sufficient to perform the unitary transformation associated with the operator  $U^\dagger(t, t_0)$  to obtain a constant transformed vector:

$$|\psi_H\rangle = U^\dagger(t, t_0)|\psi_S(t)\rangle = U^\dagger(t, t_0)U(t, t_0)|\psi_S(t_0)\rangle = |\psi_S(t_0)\rangle.$$

In the Heisenberg picture, the state vector, which is constant, is therefore equal to  $|\psi_S(t)\rangle$  at time  $t_0$ .

The transform  $A_H(t)$  of an operator  $A_S(t)$  is given by

$$A_H(t) = U^\dagger(t, t_0)A_S(t)U(t, t_0).$$

$A_H(t)$  generally depends on time, even if  $A_S$  does not. Nevertheless, there exists an interesting special case in which, if  $A_S$  is time-independent, the same is true of  $A_H$ : the case in which the system is conservative and  $[A_S, H_S] = 0$ . In this case, we have

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

If  $[A_S, H_S] = 0$ , then  $[A_S, U(t, t_0)] = 0$  so that

$$A_H(t) = U^\dagger(t, t_0)U(t, t_0)A_S = A_S.$$

The operators  $A_S$  and  $A_H$  are simply equal in this case; they indeed correspond to a constant of the motion.



When  $A_S(t)$  is arbitrary, the evolution of  $A_H(t)$  is:

$$\begin{aligned}\frac{d}{dt}A_H(t) &= -\frac{1}{i\hbar}U^\dagger(t, t_0)H_S(t)A_S(t)U(t, t_0) + U^\dagger(t, t_0)\frac{dA_S(t)}{dt}U(t, t_0) + \frac{1}{i\hbar}U^\dagger(t, t_0)A_S(t)H_S(t)U(t, t_0) \\ &= -\frac{1}{i\hbar}U^\dagger(t, t_0)H_S(t)U(t, t_0)U^\dagger(t, t_0)A_S(t)U(t, t_0) + U^\dagger(t, t_0)\frac{dA_S(t)}{dt}U(t, t_0) \\ &\quad + \frac{1}{i\hbar}U^\dagger(t, t_0)A_S(t)U(t, t_0)U^\dagger(t, t_0)H_S(t)U(t, t_0).\end{aligned}$$

Then, using the previous definitions:

$$i\hbar\frac{d}{dt}A_H(t) = [A_H(t), H_H(t)] + i\hbar\left(\frac{d}{dt}A_S(t)\right)_H. \quad (1.53)$$

- The above equation is more general than the evolution of the operator found in the chapter. Also, the evolution of the mean value:

$$\langle A \rangle(t) = \langle \psi_S(t) | A_S(t) | \psi_S(t) \rangle$$

can be calculated, since in  $\langle A \rangle(t) = \langle \phi_H | A_H(t) | \psi_H \rangle$  only  $A_H$  depends on time and therefore is obtained directly by differentiation.

- When the system is composed of a particle of mass  $m$  under a potential. Then we have (1D):

$$H_S(t) = \frac{P_S^2}{2m} + V(X_S, t), \quad \text{and therefore} \quad H_H(t) = \frac{P_H^2}{2m} + V(X_H, t).$$

Using the fact that  $[X_H, P_H] = [X_S, P_S] = i\hbar$ , we obtain that:

$$\text{Generalization of Ehrenfest theorem} \quad \begin{aligned} \frac{d}{dt}X_H(t) &= \frac{1}{m}P_H(t) \\ \frac{d}{dt}P_H(t) &= -\frac{\partial V}{\partial X}(X_H, t) \end{aligned}. \quad (1.54)$$

An advantage of Heisenberg picture is that it leads to equations formally similar to those of classical mechanics.

## 1.10 The density operator

To determine the state of a system at a given time, it suffices to perform on the system a set of measurements corresponding to a CSCO. However, in practice, the state of the system is often not perfectly determined. How can we incorporate into the formalism the incomplete information we possess about the state of the system, so that our predictions make maximum use of this partial information? We will then introduce the **density operator**.

### 1.10.1 Concept of a statistical mixture of states

When one has incomplete information about a system, one typically appeals to the concept of probability. This incomplete information is presented in the following way:

The state of this system may be either the state  $|\psi_1\rangle$  with probability  $p_1$  or  $|\psi_2\rangle$  with probability  $p_2$ . Obviously,

$$\sum_k p_k = 1.$$

We say then we are dealing with a **statistica mixture** of states  $|\psi_1\rangle, |\psi_2\rangle, \dots$  with probabilities  $p_1, p_2, \dots$ .

- The various states are not necessarily orthogonal. However, they can always be chosen normalized.
- Probabilities intervene at two different levels: a) initial information about the system, b) postulates concerning the measurement nature.
- It is impossible, in general, to describe a statistical mixture by an average state vector which would be a superposition of the states  $|\psi_k\rangle$ .

### 1.10.2 The pure case

The density operator is an **average operator** which permits a simple description of the statistical mixture of states. We will first consider the case where the state of the system is perfectly known, that is, a **pure state**. Characterizing the system by its state vector is completely equivalent to characterizing it by a certain operator acting in the state space.

#### Description by a state vector

Let be a system whose state vector is

$$|\psi(t)\rangle = \sum_n c_n(t) |u_n\rangle, \quad \text{with} \quad \sum_n |c_n(t)|^2 = 1.$$

If  $A$  is an observable with  $A_{np} = \langle u_n | A | u_p \rangle$ , then the mean value of  $A$  is

$$\langle A \rangle(t) = \langle \psi(t) | A | \psi(t) \rangle = \sum_{n,p} c_n^*(t) c_p(t) A_{np}.$$

Finally, the evolution of  $|\psi(t)\rangle$  is

$$i\hbar \partial_t |\psi(t)\rangle = H(t) |\psi(t)\rangle.$$

#### Description by a density operator

We introduce the density operator  $\rho(t)$  as

$$\text{Density operator} \quad \rho(t) = |\psi(t)\rangle \langle \psi(t)|. \quad (1.55)$$

The density operator is represented in  $\{|u_n\rangle\}$  basis by a matrix called the **density matrix** whose elements are:

$$\rho_{pn}(t) = \langle u_p | \rho(t) | u_n \rangle = c_n^*(t) c_p(t).$$

The specification of  $\rho(t)$  suffices to characterize the quantum state of the system.

First, we have the following normalization condition

$$\text{Normalization condition} \quad \sum_n |c_n(t)|^2 = \sum_n \rho_{nn}(t) = \text{Tr} [\rho(t)] = 1.$$

Secondly, the mean value of  $A$  is

$$\text{Mean value of } A \quad \langle A \rangle(t) = \sum_{n,p} \langle u_p | \rho(t) | u_n \rangle \langle u_n | A | u_p \rangle = \sum_p \langle u_p | \rho(t) | u_p \rangle = \text{Tr} [\rho(t) A].$$

Finally, the time evolution of the operator can be deduced from the Schrodinger equation above:

$$\begin{aligned} \text{Time evolution of } \rho(t) \quad \partial_t \rho(t) &= (\partial_t |\psi(t)\rangle) \langle \psi(t)| + |\psi(t)\rangle (\partial_t \langle \psi(t)|) \\ &= \frac{1}{i\hbar} H(t) |\psi(t)\rangle \langle \psi(t)| - \frac{1}{i\hbar} |\psi(t)\rangle \langle \psi(t)| H(t) \\ \partial_t \rho(t) &= \frac{1}{i\hbar} [H(t), \rho(t)]. \end{aligned} \quad (1.56)$$

The probabilities  $P(a_n)$  are then given by

$$P(a_n) = \text{Tr} [P_n \rho(t)], \quad P_n = \text{Eigensubspace of } a_n.$$

### Properties of the density operator in a pure case

In a pure case, a system can be described just as well by a density operator as by a state vector. However, the density operator presents a certain number of advantages. Using this operator eliminates the drawbacks related to the existence of an arbitrary global phase factor for the state vector. Also, by looking the above formulas we see that the expression are linear with respect to  $\rho(t)$ . Furthermore, we have

$$\rho^\dagger(t) = \rho(t), \quad \underbrace{\rho^2(t) = \rho(t), \quad \text{Tr} [\rho^2(t)] = 1}_{\text{Only for pure case}}. \quad (1.57)$$

### 1.10.3 A statistical mixture of states (non-pure case)

#### Definition of the density operator

Lets consider a system for which the various probabilities are arbitrary, on the condition that they satisfy the relations:

$$\begin{cases} 0 \leq p_1, p_2, \dots, p_k, \dots \leq 1 \\ \sum_k p_k = 1 \end{cases}$$

How does one calculate the probability  $P(a_n)$  that a measurement of the observable  $A$  will yield the result  $a_n$ ? Let  $P_k(a_n) = \langle \psi_k | P_n | \psi_k \rangle$  be the probability of finding  $a_n$  if the state vector were  $|\psi_k\rangle$ . To obtain the desired probability  $P(a_n)$ , one must weight  $P_k(a_n)$  by  $p_k$  and then sum over  $k$ :

$$P(a_n) = \sum_k p_k P_k(a_n) = \sum_k p_k \text{Tr} [\rho_k P_n] = \text{Tr} \left[ \sum_k p_k \rho_k P_n \right] = \text{Tr} [\rho P_n]. \quad (1.58)$$

We see that the linearity of the formulas which use the density operator enables us to express all physical predictions in terms of  $\rho$ .

The same density operator can be interpreted as several different statistical mixtures of pure states. This situation is sometimes described as the **multiple preparations** of the same density operator.

### General properties of the density operator

Since the coefficients  $p_k$  are real,  $\rho$  is obviously a Hermitian operator. The trace of  $\rho$  is

$$\text{Tr}[\rho] = \sum_k p_k \text{Tr}[\rho_k] \stackrel{(a)}{=} \sum_k p_k 1 = 1.$$

In (a) we saw that the trace of  $\rho_k$  (trace of pure states) is always 1. We can also generalize the formula of the mean value to statistical mixture:

$$\langle A \rangle = \sum_n a_n P(a_n) = \text{Tr} \left[ \rho \sum_n a_n P_n \right] = \text{Tr}[\rho A]. \quad (1.59)$$

Now let us calculate the time evolution of the density operator. We will assume that, unlike the state of the system, its Hamiltonian  $H(t)$  is well known. If the system at the initial time  $t_0$  has the probability  $p_k$  of being the state  $|\psi_k\rangle$ , then, at a subsequent time  $t$ , it has the same probability  $p_k$  of being in the state  $|\psi_k(t)\rangle$  given by

$$\begin{cases} i\hbar \partial_t |\psi_k(t)\rangle = H(t) |\psi_k(t)\rangle \\ |\psi_k(t_0)\rangle = |\psi_k\rangle \end{cases}$$

The density operator at the instant  $t$  will then be

$$\rho(t) = \sum_k p_k \rho_k(t), \quad \text{with} \quad \rho_k(t) = |\psi_k(t)\rangle \langle \psi_k(t)|. \quad (1.60)$$

According to the pure case,  $\rho_k(t)$  obeys the evolution equation (1.56). Thus,

$$\text{Time evolution of } \rho(t) \quad i\hbar \partial_t \rho(t) = [H(t), \rho(t)]. \quad (1.61)$$

So, we could generalize most of the equations except to the one pointed out previously. Since  $\rho$  is no longer a projector (as in the pure case), we have, in general:

$$\rho^2(t) \neq \rho(t).$$

and, consequently,

$$\text{Tr}[\rho^2] \leq 1.$$

Finally, we see from a previous equation that, for any ket  $|u\rangle$ , we have

$$\langle u | \rho | u \rangle = \sum_k p_k \langle u | \rho_k | u \rangle = \sum_k p_k |\langle u | \psi_k \rangle|^2 \implies \langle u | \rho | u \rangle \geq 0.$$

Consequently,  $\rho$  is a positive operator.

### Populations; coherences

What is the physical meaning of the matrix element  $\rho_{np}$  in the  $\{|u_n\rangle\}$  basis? We analyze first the diagonal elements  $\rho_{nn}$ :

$$\rho_{nn} = \sum_k p_k [\rho_k]_{nn} = \sum_k p_k |c_n^{(k)}|^2, \quad \text{with} \quad |c_n^{(k)}|^2 \geq 0.$$

$\rho_{nn}$  represents the average probability of finding the system in the state  $|u_n\rangle$ . That's why  $\rho_{nn}$  is called the population of the state  $|u_n\rangle$ .

A similar calculation can be carried out for non-diagonal elements  $\rho_{np}$ :

$$\rho_{np} = \sum_k p_k c_n^{(k)} c_p^{(k)*}.$$

We see that  $c_n^{(k)} c_p^{(k)*}$  is a cross term. It reflects the **interference effects** between the states  $|u_n\rangle$  and  $|u_p\rangle$  which can appear when the state  $|\psi_k\rangle$  is a coherent linear superposition of these states.  $\rho_{np}$  is the average of these cross terms, taken over all possible states of the statistical mixture. We can see that  $\rho_{nn}$  is the sum of real positive numbers, while  $\rho_{np}$  is the sum of complex numbers.

If  $\rho_{np} \neq 0$ , means that a certain coherence subsists between these states (interference effects). This is why non-diagonal elements of  $\rho$  are often called **coherences**.

- The distinction between populations and coherences obviously depends on the basis  $\{|u_n\rangle\}$  chosen in the state space. Since  $\rho$  is Hermitian, it is always possible to find an orthonormal basis  $\{|\chi_l\rangle\}$  where  $\rho$  is diagonal and can be written as

$$\rho = \sum_l \pi_l |\chi_l\rangle \langle \chi_l|.$$

Since  $\rho$  is positive and  $\text{Tr}[\rho] = 1$ , we have

$$\begin{cases} 0 \leq \pi_l \leq 1 \\ \sum_l \pi_l = 1 \end{cases}$$

$\rho$  can thus be considered to describe a statistical mixture of the states  $|\chi_l\rangle$  with the probabilities  $\pi_l$  (no coherence between the states  $|\chi_l\rangle$ ).

- If the kets  $|u_n\rangle$  are eigenvectors of the Hamiltonian  $H$  (assumed time-independent), the populations are constant, and the coherences oscillates at the Bohr frequencies of the system.
- $\rho$  can have coherences only between states whose populations are not zero ( $\rho_{nn}\rho_{pp} \geq |\rho_{np}|^2$ ).

#### 1.10.4 Separate description of part of a physical system. Concept of a partial trace

# Formula sheet

## 1.10.5 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\}}$ $A_{\{v\}} = \mathbb{M}^{\dagger} A_{\{u\}} \mathbb{M}$

## 1.10.6 Basis

Quantity	Discrete basis (sum over $j, k$ )	Continuous basis (integrate over $\beta, \beta'$ )
$\mathbb{1}$	$= \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
$X$	$x$	$i\hbar \partial/\partial p$
$P_x$	$-i\hbar \partial/\partial x$	$p$
$ 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 $	$\int_{-\infty}^{\infty} dx \varphi^*(x) \psi(x) = \int_{-\infty}^{\infty} dp \tilde{\varphi}^*(p) \tilde{\psi}(p)$
$\psi(x)$ real: $[\tilde{\psi}(p)]^* = \tilde{\psi}(-p)$	$\psi(x)$ 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 block submatrix.
- The eigenpairs allows you to diagonalize  $A = V\Lambda V^{-1}$  in the eigenbasis, where  $V = [\mathbf{u}_1|\mathbf{u}_2|\dots]$ ,  $\Lambda = \text{diag}(\lambda_1, \lambda_2, \dots)$ , and  $A|\mathbf{u}_i\rangle = \lambda_i|\mathbf{u}_i\rangle$ . In the eigenbasis we can do  $F(A) = VF(\Lambda)V^{-1}$ .
- When  $A$  is Hermitian,  $V$  is unitary:  $V^{-1} = V^{\dagger}$ .

$ \begin{aligned} [A, B] &= -[B, A] \\ [A, B]^\dagger &= [B^\dagger, A^\dagger] \\ [AB, CD] &= A[B, C]D + AC[B, D] + [A, C]DB + C[A, D]B \\ [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 \\ [H, P] &= i\hbar \frac{dV(X)}{dX} \end{aligned} $	$ \begin{aligned} [A + B, C + D] &= [A, C] + [A, D] + [B, C] + [B, D] \\ [F(A), A] &= 0 \\ [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} \\ [H, X] &= -\frac{i\hbar}{m} P \\ \langle \varphi_n   [A, H]   \varphi_n \rangle &= 0, \quad \forall A \end{aligned} $
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- If the matrix is diagonal, the exponential acts directly onto the elements.
- The evolution operator is  $U = e^{-iHt/\hbar}$  and it evolves the state by matrix multiplication  $U|\psi\rangle$ .
- The eigenequation show you the relation of the eigenvectors that must be considered to construct the eigenvectors of the eigenbasis:  $A|u_i\rangle = \lambda|u_j\rangle$ . Its matrix representation is  $\lambda$  in the  $ji$  position.
- 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  $|\psi\rangle$  or  $\langle\psi|$ .
- In the operation  $|u_i\rangle\langle u_j|$ , the element will be located at  $ij$  in the matrix.
- Conservative= $H$  time-independent, Stationary state= $|\psi\rangle$  projects in a single eigenstate of  $H$ .
- Constant of motion= $A$  time-independent and  $[A, H] = 0$ .

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# Index

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Compatible operators, 15

Ehrenfest's theorem, 18

Evolution operator, 21

Good quantum numbers, 20

Mean value of an observable, 13

Stationary states, 19

