

Chapter 2

Quantum Mechanical Background

Quantum mechanics is certainly one of the most successful theories in science. It has deeply influenced many areas of pure and applied physics and pervades many branches of science, from physics, matter sciences, computer science to chemistry and even to molecular biology. However, quantum mechanics has to face several conceptual difficulties of which most relate to the process of quantum measurement and its randomness so that, almost one century after its birth, a complete consensus has still not been reached concerning the interpretation of the theory and its foundations.

Quantum mechanics is also known to be *counter-intuitive* and to lead to representations of physical phenomena very different from our daily experience, such as *superposition*, *entanglement* and *non-locality*. To pinpoint this microscopic “quantum strangeness”, the fathers of the quantum theory, especially Einstein and Bohr, resorted to “*thought experiments*” involving the manipulations of isolated particles. These experiments, which were believed to remain virtual, have now been performed (see “Exploring the Quantum” by Haroche and Raimond [1]) and may help shed light on the conceptual difficulties mentioned above. In their turn, they may also raise other intriguing issues such as, for instance, the connection between quantum and classical physics. Indeed, macroscopic systems, i.e. systems directly accessible to our senses, never display non-locality and other strange features of quantum mechanics such as *state superposition* (Schrödinger’s cat) or *quantum interference*.

A nice, lively and non-technical overview of the major interpretations and strangeness of quantum mechanics can be found in “Beyond measure” by Baggot [2]. More in-depth and technical discussions are given in “Do we really understand Quantum Mechanics?” by Laloë [3].

It is perhaps also worth mentioning that, by casting doubts on fundamental concepts such as space, material objects, and causality quantum mechanics demands serious *reconsideration* of most of traditional philosophy and has become a central issue in the realm of the *philosophy of science*. A huge amount of literature exists on the subject and we will only mention here two examples: “On Physics and Philosophy” by d’Espagnat [4] and “Making Sense of Quantum Mechanics” by Bricmont [5].

Nevertheless, *in spite of all these conceptual difficulties, the extraordinary feature of quantum mechanics is that, although we do not understand it nor know how to interpret it, we can apply it* and, by means of the rules of calculation it inspires, compute *properties of matter with unparalleled accuracy*. However, in the present book, we will adopt what can be viewed as a *pragmatic approach* in which quantum mechanics is regarded as an operational theory designed to predict the outcomes of measurements on physical systems under well-defined conditions.

The purpose of the present chapter is not to provide a general and detailed introduction to quantum mechanics, which is available in most textbooks, e.g. Refs. [6–15]. Our purpose here is merely to provide a *quantum mechanical background* with emphasis on the concepts and rules needed for the various topics covered in the book. (for a lively and pedagogical further reading see “Lectures on Quantum Mechanics” by Basdevant [16].)

2.1 General Principles

2.1.1 Wavefunctions

In quantum mechanics, the *state of a system*, at a given time t , parametrized by a set of coordinates $\mathbf{R}$, is completely determined by a complex *wavefunction*, $\Psi(\mathbf{R}, t)$ [10]. In our case, the system will often be a *molecular system* in the wider sense of the term, and the coordinates $\mathbf{R}$, a set of *generalized or curvilinear coordinates well-adapted* to the description and the evolution in time of the molecular and chemical processes under consideration. According to the standard interpretation of quantum mechanics, the square of the modulus of $\Psi(\mathbf{R}, t)$,

$$|\Psi(\mathbf{R}, t)|^2 = \Psi^*(\mathbf{R}, t)\Psi(\mathbf{R}, t), \quad (2.1)$$

has the meaning of a *probability density*. The *probability* of finding the system in the volume $d\mathbf{R}$ around the point $\mathbf{R}$ at time t , is given by

$$d\mathcal{P}(\mathbf{R}, t) = |\Psi(\mathbf{R}, t)|^2 d\mathbf{R}. \quad (2.2)$$

The wavefunction $\Psi(\mathbf{R}, t)$ is also called the *probability amplitude* of finding the system at point $\mathbf{R}$. It is square integrable and, in view of the probabilistic interpretation, must be normalized to unity¹:

$$\int |\Psi(\mathbf{R}, t)|^2 d\mathbf{R} = 1. \quad (2.3)$$

¹In the following, $\int$ denotes the integral over the complete domain of definition.

2.1.2 Superposition Principle

Another property of wavefunctions, regarded as a fundamental principle of quantum mechanics, is the *superposition principle*: it means that, if $\Psi_1(\mathbf{R}, t)$ and $\Psi_2(\mathbf{R}, t)$ describe possible states for the system, any linear combination

$$\Psi(\mathbf{R}, t) = c_1 \Psi_1(\mathbf{R}, t) + c_2 \Psi_2(\mathbf{R}, t), \quad (2.4)$$

where c_1 and c_2 are arbitrary complex coefficients, also represents a possible state. The additivity of probability *amplitudes* is at the origin of *interference phenomena* in quantum mechanics (see Eq. (2.38) below). Moreover, from a more theoretical perspective, this additivity property hints to the fact that the set of all the possible wavefunctions of a given system has the properties of a *linear vector space* $\mathcal{E}$ (see below).

The non-classical aspect of the superposition principle is illustrated by Schrödinger's famous cat, which can be alive and dead simultaneously. In other words, *Schrödinger's cat* can be in a *coherent superposition* of both a dead state and an alive state. These two states can interfere to create new behaviors that cannot be observed for a cat that is either alive or dead. For instance, let us consider an assembly of, let us say, one thousand Schrödinger's cats. This assembly is not constituted of cats that are either dead or alive but of one thousand cats where the dead and alive aspects interact to create a completely different behavior. Schrödinger's cat can be seen as a *paradox* only because the cat is a large-scale system and creating a coherent superposition for a cat is not realistic.

2.1.3 Measurements of Physical Quantities

One of the most intriguing features of quantum mechanics is, as indicated by its name, the hypothesis of *quantization*. This notion implies that, under particular conditions, physical observables measured experimentally can only take certain discrete values. More precisely, in quantum mechanics, physical quantities measured experimentally can only take a *restricted set of values* that can be discrete or continuous or a mixture of both.

This is the reason why, whereas in classical mechanics the physical observables are represented by functions of time such as position, in quantum mechanics, to each physical quantity $\mathcal{A}$, we associate an observable $\hat{A}$, which is a *linear Hermitian operator* acting in the space $\mathcal{E}$ of wavefunctions called a *Hilbert space*.

More explicitly, let us define in the space $\mathcal{E}$ a *Hermitian scalar product*² of two wavefunctions $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$ as follows

²Equation (2.5) is also known as the *overlap between the wavefunctions* $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$.

$$\int \Phi^*(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R} = \langle \Phi | \Psi \rangle, \quad (2.5)$$

where the so-called Dirac *bracket notation* is introduced. This bracket notation is very elegant and allows, among other things, to avoid to explicitly specify the coordinates, $\mathbf{R}$, their conjugate momenta $\mathbf{P}$, or any other set of coordinates, used to describe the system. Combined with the superposition principle, this leads naturally to considering $|\Psi\rangle$, called a “ket”, as a *vector* of space $\mathcal{E}$, and $\langle\Phi|$ called a “bra” as a linear form³ that acts on the ket $|\Psi\rangle$ to yield the “bracket” $\langle\Phi|\Psi\rangle$, which, being a scalar product, is generally a complex number.

$|\Psi\rangle$ and $|\Phi\rangle$ are quantum *state vectors* corresponding to the “ $\mathbf{R}$ representation” wavefunctions $\Psi(\mathbf{R})$ and $\Phi(\mathbf{R})$. The *normalization condition* of Eq. (2.3) now reads

$$\langle\Psi|\Psi\rangle = 1, \quad (2.6)$$

and the *orthogonality condition*

$$\langle\Phi|\Psi\rangle = \int \Phi^*(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R} = 0 \quad (2.7)$$

may be regarded as an extension of the geometrical notion of orthogonality to state vectors and wavefunctions.

An *operator* $\hat{A}$ transforms any given vector $|\Psi\rangle$ into another vector $|\Psi'\rangle = |\hat{A}\Psi\rangle = \hat{A}|\Psi\rangle$. When acting on a vector $\alpha|\Psi\rangle + \beta|\Phi\rangle$, where α and β are complex numbers, such as

$$\hat{A}(\alpha|\Psi\rangle + \beta|\Phi\rangle) = \alpha\hat{A}|\Psi\rangle + \beta\hat{A}|\Phi\rangle. \quad (2.8)$$

the operator is called a *linear operator*. We will work only with linear operators. *Matrix elements* of an operator $\hat{A}$ are written as

$$\langle\Psi|\hat{A}|\Phi\rangle = \langle\Psi|\hat{A}\Phi\rangle = \int \Psi^*(\mathbf{R})\hat{A}\Phi(\mathbf{R})d\mathbf{R}. \quad (2.9)$$

³In a finite Hermitian space $\mathbb{C}^n$, the “kets” are the column matrices $|u\rangle = \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_n \end{bmatrix}$ and the “bra” are the row matrices $\langle v| = [v_1^* v_2^* \dots v_n^*]$ so that $\langle v|u\rangle = \sum_{i=1}^n v_i^* u_i$ is a matrix product.

The *product* of two operators $\hat{A}$ and $\hat{B}$ is defined as $(\hat{A}\hat{B})|\Psi\rangle = \hat{A}(\hat{B}|\Psi\rangle)$. It is interesting to note that multiplying a ket by a bra, $|\Psi\rangle\langle\Phi|$ is an operator.⁴ Indeed, applied to a vector $|\varphi\rangle$, it yields another vector: $|\Psi\rangle\langle\Phi|\varphi\rangle = \langle\Phi|\varphi\rangle|\Psi\rangle$, where $\langle\Phi|\varphi\rangle$ is a complex number. In particular, $\hat{\Pi}_\Psi = |\Psi\rangle\langle\Psi|$ is the *projection* operator onto $|\Psi\rangle$, since

$$\hat{\Pi}_\Psi^2 = |\Psi\rangle\langle\Psi|\Psi\rangle\langle\Psi| = |\Psi\rangle\langle\Psi| = \hat{\Pi}_\Psi \quad (2.10)$$

holds, which shows that $\hat{\Pi}_\Psi$ is a projector, and since

$$\hat{\Pi}_\Psi|\Psi\rangle = |\Psi\rangle\langle\Psi|\Psi\rangle = |\Psi\rangle \quad (2.11)$$

holds, which shows that the projector projects onto $|\Psi\rangle$. Note that a normalized $|\Psi\rangle$ is assumed.

The *commutator* of two operators $\hat{A}$ and $\hat{B}$ is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \quad (2.12)$$

When $[\hat{A}, \hat{B}] = 0$, which implies $\hat{A}\hat{B} = \hat{B}\hat{A}$, the two operators are said to *commute*.

For each linear operator $\hat{A}$, there exists an *adjoint operator*, $\hat{A}^\dagger$, defined as follows:

$$\langle\Psi|\hat{A}^\dagger|\Phi\rangle = \langle\hat{A}\Psi|\Phi\rangle = \langle\Phi|\hat{A}|\Psi\rangle^* \quad (2.13)$$

or, in integral form, with wavefunctions

$$\begin{aligned} \langle\Psi|\hat{A}^\dagger|\Phi\rangle &= \int \Psi^*(\mathbf{R})\hat{A}^\dagger\Phi(\mathbf{R})d\mathbf{R} = \int (\hat{A}\Psi(\mathbf{R}))^*\Phi(\mathbf{R})d\mathbf{R} \\ &= \left(\int \Phi^*(\mathbf{R})\hat{A}\Psi(\mathbf{R})d\mathbf{R} \right)^* = \langle\Phi|\hat{A}|\Psi\rangle^*. \end{aligned} \quad (2.14)$$

An operator $\hat{A}$ is *Hermitian* if

$$\hat{A}^\dagger = \hat{A}. \quad (2.15)$$

If $\hat{A}$ is Hermitian, its *expectation value*, i.e. $\langle\Psi|\hat{A}|\Psi\rangle$ for a given state vector $|\Psi\rangle$, is real. Indeed, in view of Eq. (2.14) and since $\hat{A}^\dagger = \hat{A}$

$$\langle\Psi|\hat{A}|\Psi\rangle^* = \langle\Psi|\hat{A}^\dagger|\Psi\rangle = \langle\Psi|\hat{A}|\Psi\rangle. \quad (2.16)$$

⁴In a finite Hermitian space $\mathbb{C}^n$, $|u\rangle\langle v| = \begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_n \end{bmatrix} [v_1^* v_2^* \dots v_n^*] = \begin{bmatrix} u_1 v_1^* & u_1 v_2^* & \dots & u_1 v_n^* \\ u_2 v_1^* & u_2 v_2^* & \dots & u_2 v_n^* \\ \vdots & \vdots & \ddots & \vdots \\ u_n v_1^* & u_n v_2^* & \dots & u_n v_n^* \end{bmatrix}$, which is a $(n \times n)$ matrix, i.e. an operator in $\mathcal{C}^n$.

A *nonzero* vector $|\varphi_k\rangle$ is said to be an *eigenvector* of an operator $\hat{A}$ if

$$\hat{A}|\varphi_k\rangle = a_k|\varphi_k\rangle, \quad (2.17)$$

and a_k is the *eigenvalue* associated with this eigenvector. The set $\{a_k\}$ is called the *spectrum* of $\hat{A}$. For simplicity, we assume the spectrum to be discrete and non-degenerate (i.e. there are no two or more equal eigenvalues).

If $\hat{A}$ is Hermitian, the eigenvalues a_k are real and the eigenvectors corresponding to different eigenvalues are orthogonal. Thus, taking eigenvectors normalized to unity, we have

$$\langle\varphi_k|\varphi_l\rangle = \delta_{kl}, \quad (2.18)$$

where δ_{kl} is the *Kronecker delta*. In addition, the set $\{\varphi_k\}$ of normalized eigenvectors forms a complete set of orthonormal basis vectors (*spectral theorem*), i.e. any state vector $|\Psi\rangle$ can be expanded as follows

$$|\Psi\rangle = \sum_k c_k |\varphi_k\rangle, \quad (2.19)$$

or, in terms of wavefunctions,

$$\Psi(\mathbf{R}) = \sum_k c_k \varphi_k(\mathbf{R}), \quad (2.20)$$

where the c_k are complex coefficients. In fact,

$$c_k = \langle\varphi_k|\Psi\rangle = \int \varphi_k^*(\mathbf{R}) \Psi(\mathbf{R}) d\mathbf{R}, \quad (2.21)$$

and, since $\Psi(\mathbf{R})$ is normalized to unity, i.e. $\langle\Psi|\Psi\rangle = 1$,

$$\sum_k |c_k|^2 = 1. \quad (2.22)$$

If two observables *commute*, there exists a basis of *eigenvectors common* to the two operators.

To summarize: to each *physical quantity* $\mathcal{A}$ corresponds an *observable* $\hat{A}$ that is a Hermitian linear operator acting in the space of wavefunctions $\mathcal{E}$, and characterized by its spectrum, i.e. the set $\{a_k\}$ of its eigenvalues and the set $\{\varphi_k(\mathbf{R})\}$ of the corresponding normalized eigenfunctions, which constitute an orthonormal basis set of $\mathcal{E}$ (spectral theorem).

We are now ready to state⁵ the *measurement principles* of quantum mechanics:

(a) In the measurement of a physical quantity $\mathcal{A}$, the only possible results of the measurement are the eigenvalues a_k of the corresponding observable $\hat{A}$ (it is also known as the *quantization principle*).

(b) Owing to the *spectral theorem*, the wavefunction *before* the measurement can be expressed in terms of the normalized eigenfunctions of $\hat{A}$:

$$\Psi(\mathbf{R}) = \sum_k c_k \varphi_k(\mathbf{R}) . \quad (2.23)$$

When the measurement occurs, the *probability* of finding the value a_k as *result* is

$$\mathcal{P}(a_k) = |c_k|^2 = |\langle \varphi_k | \Psi \rangle|^2 . \quad (2.24)$$

The above equation is also known as *Born's probability rule*.

(c) Immediately after the measurement of the physical quantity $\mathcal{A}$ has been performed and *has given the result* a_k , the new state wavefunction of the system is the (normalized) eigenfunction $\varphi_k(\mathbf{R})$. This “instantaneous” change from $\Psi(\mathbf{R})$ to $\varphi_k(\mathbf{R})$ is known as the *reduction of the wavepacket* or *wavefunction collapse*. According to the standard interpretation of quantum mechanics, this wavefunction collapse is due to the interaction between the system and the measuring apparatus.⁶

As already briefly mentioned, for a given wavefunction $\Psi(\mathbf{R})$, the *expectation value* of any physical quantity $\mathcal{A}$ is given by

$$\int \Psi^*(\mathbf{R}) \hat{A} \Psi(\mathbf{R}) d\mathbf{R} = \langle \Psi | \hat{A} | \Psi \rangle . \quad (2.25)$$

Introducing Eq. (2.23) into Eq. (2.25) yields

$$\begin{aligned} \int \Psi^*(\mathbf{R}) \hat{A} \Psi(\mathbf{R}) d\mathbf{R} &= \sum_k \sum_l c_k^* c_l \int \varphi_k^*(\mathbf{R}) \hat{A} \varphi_l(\mathbf{R}) d\mathbf{R} \\ &= \sum_k \sum_l c_k^* c_l \int \varphi_k^*(\mathbf{R}) a_l \varphi_l(\mathbf{R}) d\mathbf{R} \\ &= \sum_k \sum_l c_k^* c_l a_l \int \varphi_k^*(\mathbf{R}) \varphi_l(\mathbf{R}) d\mathbf{R} \\ &= \sum_k \sum_l c_k^* c_l a_l \delta_{kl} , \end{aligned} \quad (2.26)$$

⁵We do it mainly in terms of wavefunctions since the “ $\mathbf{R}$ representation” will be predominantly used in the present book.

⁶The mechanism and meaning of the wavepacket collapse is a difficult and much debated topic in quantum mechanics. For an introduction see, for instance Chap. 8 of Ref. [3].

so that

$$\langle \Psi | \hat{A} | \Psi \rangle = \sum_l |c_l|^2 a_l = \sum_l \mathcal{P}(a_l) a_l , \quad (2.27)$$

which is the usual definition of the *expectation value* in standard probability theory. As pointed out in Chap. 9 of Ref. [3], in the majority of experiments, what is really observed is the sum over a very large number of particles of one individual microscopic observable (sum of atomic dipoles for instance), which is accurately described by the *average value of this observable*, i.e. the *expectation value* (see Eq. (2.27)).

2.1.4 Time Evolution Principle and Schrödinger Equation

As long as the system does not undergo any observation, its time evolution is postulated to be given by the *time-dependent Schrödinger equation* (TDSE):

$$\hat{H}(t)\Psi(\mathbf{R}, t) = i\hbar \frac{\partial \Psi(\mathbf{R}, t)}{\partial t} , \quad (2.28)$$

with $\hbar = \frac{h}{2\pi}$, the *reduced Planck constant*. The operator $\hat{H}(t)$ is the *energy observable* or *Hamiltonian operator*, which may or may not depend on time.

If the *Hamiltonian operator is time-independent*, i.e. if the system is isolated, one may solve the eigenvalue equation

$$\hat{H}\Psi_n(\mathbf{R}) = E_n \Psi_n(\mathbf{R}) , \quad (2.29)$$

which is known as the *time-independent Schrödinger equation* (TISE).

Equation (2.28) can then be formally solved as:

$$\Psi(\mathbf{R}, t) = e^{-i\hat{H}t/\hbar} \Psi(\mathbf{R}, t=0) , \quad (2.30)$$

where $e^{-i\hat{H}t/\hbar}$ is known as the *evolution operator*.

Then, two cases must be distinguished:

(i) At a time of reference, say $t = 0$, the wavefunction is equal to one of the eigenfunctions given by Eq. (2.29):

$$\Psi(\mathbf{R}, t=0) = \Psi_n(\mathbf{R}) . \quad (2.31)$$

Inserting Eq. (2.31) into Eq. (2.30) yields

$$\Psi(\mathbf{R}, t) = e^{-iE_n t/\hbar} \Psi_n(\mathbf{R}) . \quad (2.32)$$

The time dependence of such a state is *periodic*, with angular frequency $\omega_n = E_n/\hbar$. As regards the *probability density*,

$$\begin{aligned} |\Psi(\mathbf{R}, t)|^2 &= \Psi^*(\mathbf{R}, t) \Psi(\mathbf{R}, t) \\ &= e^{iE_n t/\hbar} \Psi_n^*(\mathbf{R}) e^{-iE_n t/\hbar} \Psi_n(\mathbf{R}) \\ &= \Psi_n^*(\mathbf{R}) \Psi_n(\mathbf{R}) = |\Psi_n(\mathbf{R})|^2. \end{aligned} \quad (2.33)$$

Thus, the probability density does not depend on time. In other words, the system does not evolve and is said to be in a *stationary state*. To each stationary state corresponds a definite value of the energy of the system, E_n .

(ii) At $t = 0$, the wavefunction is a linear combination of the eigenfunctions given by Eq. (2.29). Such a linear combination is often called a *coherent superposition* or also a *wavepacket*.

In other words,

$$\Psi(\mathbf{R}, t = 0) = \sum_n c_n \Psi_n(\mathbf{R}), \quad (2.34)$$

in the *discrete case* and

$$\Psi(\mathbf{R}, t = 0) = \int c(E) \Psi_E(\mathbf{R}) dE, \quad (2.35)$$

in the *continuous case*. For systems with both discrete and continuous portions in their spectra the expression is a sum of Eqs. (2.34) and (2.35).

In Eq. (2.34),

$$c_n = \int \Psi_n^*(\mathbf{R}) \Psi(\mathbf{R}, t = 0) d\mathbf{R}, \quad (2.36)$$

is the *overlap* between the wavefunction and the eigenfunction $\Psi_n(\mathbf{R})$ (see Eq. (2.21)).

Equation (2.34) can be seen as a particular case of the aforementioned superposition principle. The physical situation described by the wavefunction of Eq. (2.34) has no classical counterpart. In classical mechanics, the system has a single well-defined energy. On the other hand, if the energy of the quantum system described by Eq. (2.34) is measured, several different outcomes, E_n , are possible. Quantum mechanics can only predict *the probability of measuring the value E_n , which is equal to $|c_n|^2$* (see Eq. (2.24) the Born probability rule). As already explained, if the energy is measured and if the value $E_{n'}$ is obtained, it means that the wavefunction $\sum_n c_n \Psi_n(\mathbf{R})$ has been reduced to $\Psi_{n'}(\mathbf{R})$. Thus, the quantum system described by Eq. (2.34) has no well-defined energy. However, the *expectation value* of the Hamiltonian operator, $\langle \Psi | \hat{H} | \Psi \rangle$, gives the mean energy that is constant over time for an isolated system (*law of energy conservation*).

Now, inserting Eq. (2.34) into Eq. (2.30), we obtain

$$\begin{aligned}
 \Psi(\mathbf{R}, t) &= e^{-i\hat{H}t/\hbar} \sum_n c_n \Psi_n(\mathbf{R}), \\
 &= \sum_n c_n e^{-i\hat{H}t/\hbar} \Psi_n(\mathbf{R}), \\
 &= \sum_n c_n e^{-iE_n t/\hbar} \Psi_n(\mathbf{R}).
 \end{aligned} \tag{2.37}$$

This wavefunction is no longer stationary and the probability density $|\Psi(\mathbf{R}, t)|^2$ exhibits an *interference pattern*. Indeed

$$\begin{aligned}
 |\Psi(\mathbf{R}, t)|^2 &= \Psi^*(\mathbf{R}, t) \Psi(\mathbf{R}, t) \\
 &= \left(\sum_l c_l^* e^{iE_l t/\hbar} \Psi_l^*(\mathbf{R}) \right) \left(\sum_n c_n e^{-iE_n t/\hbar} \Psi_n(\mathbf{R}) \right) \\
 &= \sum_l \sum_n c_l^* c_n e^{-i(E_n - E_l)t/\hbar} \Psi_l^*(\mathbf{R}) \Psi_n(\mathbf{R}) \\
 &= \sum_n |c_n|^2 |\Psi_n(\mathbf{R})|^2 + \sum_n \sum_{l, l \neq n} c_l^* c_n e^{-i(E_n - E_l)t/\hbar} \Psi_l^*(\mathbf{R}) \Psi_n(\mathbf{R}).
 \end{aligned} \tag{2.38}$$

Equation (2.38) has thus two terms:

- The first term, which does not depend on time.
- The second one called the “*interference term*” is the result of the interferences between the different eigenstates. The *probability density* now *depends on time* and does so through the second term only. Again, this originates from having a *coherent superposition* of eigenstates with different energies. Such a wavefunction is often referred to as a *wavepacket*. In practice, a wavepacket often corresponds to a wavefunction that is localized in space.

Creating experimentally such a coherent superposition and preserving it is a difficult task. Since a system is never isolated, it interacts with its environment that dissipates the quantum coherence: thus, a *loss of coherence* between the different quantum states occurs and is called *quantum decoherence*. The quantum interference terms vanish locally, i.e. in the system, and the latter is formally equivalent to a classical statistical mixture or an “*incoherent*” mixture of states rather than a single coherent quantum superposition of them. The effect of the environment is not included in the Hamiltonian operator introduced above and for which the eigenstates have been defined.

Let us return to our assembly of one thousand Schrödinger’s cats. After interaction with the environment the assembly of one thousand cats simply corresponds to a statistical assembly of roughly five hundred cats that are dead and five hundred cats that are alive. The different states do not interact or “interfere” together to create non-classical behaviors. Since a cat is a large-scale system, the interaction

with the environment will occur extremely fast. Therefore, even if it were possible to generate such a quantum superposition of cats, the quantum decoherence would be so fast that it would be impossible to measure the corresponding quantum properties. The difficulty and the importance of creating a quantum superposition has been emphasized by the 2012 Nobel prize in Physics awarded to Serge Haroche and David Jeffrey Wineland. For instance, Serge Haroche was able to create a coherent state of light in a cavity cooled to 0.8 K and perform a step-by-step measurement of the wavefunction collapse by interaction with circular Rydberg atoms of Rubidium, i.e. excited atoms with electrons that have very high principal quantum numbers. He produced actual movies of the decoherence process in progress until the system became a Fock state of well-defined energy with a definite number of photons [17, 18].

The *systematic control of quantum coherence* is seen as one of the main challenges in basic energy sciences since such a control may lead to highly desirable materials and devices such as *quantum computers* [19]. In the same manner, the exploitation of this quantum coherence in molecular processes may lead to a *more efficient chemistry*. Indeed, in traditional chemistry, the quantum states involved in the chemical process are, in general, populated in an incoherent way described as a “*mixed state*” in quantum statistical mechanics. Since the invention of lasers, which emit light *coherently* thanks to the process of stimulated emission, it is possible to create coherent superpositions of molecular quantum states. Such coherent superpositions are called a “*pure state*” in quantum statistical mechanics and their systematic use might strongly increase the efficiency and the control of the corresponding chemical processes and at a much lower energy cost. In practice, quantum coherence can be preserved during a time that is sufficient for a complete rearrangement of the molecular system. In this context and as aforementioned in the introduction, it is worth noting that recent experiments provided observation of *long-lived electronic quantum coherence*, after excitation by laser pulses, for energy transfer processes in light-harvesting complexes of biological systems such as photosynthetic systems at ambient temperature and in the condensed phase [20].

These coherent superpositions correspond to what we called a *wavepacket* above. *The central object of study in this book is the use of wavepackets in the context of chemistry.* As explained, molecular wavepackets can be created by lasers and exploited to guide chemical processes. In addition, from their intrinsic mathematical nature, wavepackets are very efficient tools for *theoreticians to compute several physical observables, independently of the possibility to create the former experimentally*. In simulations, artificial molecular wavepackets can be generated with the MCTDH package for instance. Their propagations can lead to quantities such as *absorption spectra* or *cross sections* including all the most subtle quantum effects that may occur in molecular processes.

2.2 Observables and Correspondence Principle

We have seen in the previous section that, in order to treat quantum mechanically a physical quantity $\mathcal{A}$ pertaining to a given system, we have to rely on a corresponding observable $\hat{A}$, which is a Hermitian linear operator acting on the wavefunctions that define the states of the system. *What are the rules to be used to carry out the correspondence $\mathcal{A} \rightarrow \hat{A}$?*

2.2.1 Observables Corresponding to Common Physical Quantities

Let us begin by considering a particle of mass m , of (Cartesian) *position coordinates* $\mathbf{r} = (x, y, z)$ and *classical momentum* $\mathbf{P} = (P_x, P_y, P_z)$. Concerning the corresponding *position observable* $\hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z})$, it is simply a multiplication of the wavefunction by $\mathbf{r} = (x, y, z)$. Concerning the momentum properties, the corresponding *momentum observable* is⁷

$$\begin{aligned}\hat{\mathbf{P}} = (\hat{P}_x, \hat{P}_y, \hat{P}_z) &= (-i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z}) \\ &= -i\hbar \nabla.\end{aligned}\tag{2.39}$$

Concerning other physical properties that in classical mechanics are functions $A(\mathbf{r}, \mathbf{P})$ of the position and momentum variables, a *correspondence principle* is introduced, which consists in choosing for quantum mechanics the same functions of the position and momentum observables. So, to the classical quantity $A(\mathbf{r}, \mathbf{P})$ corresponds the observable $\hat{A}(\hat{\mathbf{r}}, \hat{\mathbf{P}})$. See Table 2.1 for the expressions of the observables corresponding to common physical quantities. For instance, the observable corresponding to the classical *angular momentum*⁸ $\mathbf{L} = \mathbf{r} \times \mathbf{P}$ is given by $\hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla$ that is

$$\hat{L}_x = -i\hbar(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y}),\tag{2.40}$$

and the cyclic permutations

$$\begin{aligned}\hat{L}_y &= -i\hbar(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z}) \\ \hat{L}_z &= -i\hbar(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}).\end{aligned}\tag{2.41}$$

⁷ ∇ denotes the gradient operator, which here is defined as a row vector. See also Sect. 3.2.3 for a more comprehensive definition of gradient operators.

⁸In the present book, $\times$ denotes the vector product.

Table 2.1 Observables corresponding to common physical quantities [12, 13]

Physical quantity $\mathcal{A}$	Observable $\hat{A}$
Position $x, y, z, \mathbf{r}$	Multiplication by $x, y, z, \mathbf{r}$
Momentum $P_x, P_y, P_z, \mathbf{P}$	$\hat{P}_x = -i\hbar \frac{\partial}{\partial x}, \hat{P}_y = -i\hbar \frac{\partial}{\partial y}, \hat{P}_z = -i\hbar \frac{\partial}{\partial z},$ $\hat{\mathbf{P}} = -i\hbar \nabla$ (gradient)
Kinetic energy $T = \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2)$	$\hat{T} = -\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2})$
$T = \frac{1}{2m}\mathbf{P}^2$	$\hat{T} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\Delta$ (Laplacian)
Potential energy $V(\mathbf{r})$	Multiplication by $V(\mathbf{r})$
Total energy $E = T + V(\mathbf{r})$	Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})$
Angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{P}$	$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{P}} = -i\hbar \mathbf{r} \times \nabla$

Let us notice and recall that the position and momentum observables, $\hat{\mathbf{r}}$ and $\hat{\mathbf{P}}$, do not commute. Indeed,

$$\hat{x}\hat{P}_x\Psi = \hat{x}(\hat{P}_x\Psi) = -ix\hbar\frac{\partial\Psi}{\partial x}, \quad (2.42)$$

and

$$\hat{P}_x\hat{x}\Psi = \hat{P}_x(\hat{x}\Psi) = -i\hbar\frac{\partial}{\partial x}(x\Psi) = -ix\hbar\frac{\partial\Psi}{\partial x} - i\hbar\Psi. \quad (2.43)$$

Introducing the *commutator* of two operators $\hat{A}$ and $\hat{B}$ defined above

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}, \quad (2.44)$$

we see that

$$[\hat{x}, \hat{P}_x] = \hat{x}\hat{P}_x - \hat{P}_x\hat{x} = i\hbar\hat{I}, \quad (2.45)$$

where $\hat{I}$ is the *identity operator*. Moreover, it is clear that $\hat{x}$ and $\hat{P}_y$ commute. Denoting the components of $\hat{\mathbf{r}}$ and $\hat{\mathbf{P}}$ by $\hat{x}_i$ and $\hat{P}_i$, $i = 1, 2, 3$, we obtain the well-known *fundamental commutation relations*:

$$[\hat{x}_i, \hat{x}_j] = [\hat{P}_i, \hat{P}_j] = 0, \quad (2.46)$$

and

$$[\hat{x}_i, \hat{P}_k] = i\hbar\delta_{ik}. \quad (2.47)$$

Owing to these fundamental commutation relations, it is worth noting that the correspondence between physical quantities and operators is simple when the quantity is a function of either the position or the momentum alone. In contrast, when the quantity is a function of both $\hat{\mathbf{r}}$ and $\hat{\mathbf{P}}$, some care has to be taken since products of (non commuting) operators depend in general on the order in which they are written.

The correspondence principle is rather easily extended to the case of a collection of particles such as molecular systems made up of nuclei and electrons. We will describe these systems with the help of a set $\mathbf{R}$ of *well-adapted curvilinear coordinates* and their canonical conjugate momenta $\mathbf{P}$. Particular attention will be paid to the way of applying the correspondence principle to $T(\mathbf{R}, \mathbf{P})$, the classical Hamiltonian kinetic energy, where the ordering problem for $\hat{\mathbf{R}}$ and $\hat{\mathbf{P}}$ mentioned above will crop up.

The properties and explicit expressions of the momentum operators $\hat{\mathbf{P}}$, corresponding to the classical momenta conjugate to the generalized coordinates $\mathbf{R}$ will be detailed in Chap. 6. Concerning the energy observable, the Hamiltonian operator $\hat{H}(\mathbf{R}) = \hat{T}(\mathbf{R}) + \hat{V}(\mathbf{R})$ describing a confined system, i.e. a *bound system*, has a *discrete spectrum*. In contrast, for *unbound systems*, the energy spectrum is *continuous*.

2.2.2 Angular Momentum Operators

We now recapitulate some properties of the angular momentum operators. For a more detailed account see for instance Refs. [7, 9, 10, 13].

The *angular momentum observable* of a particle according to the correspondence principle (see Table 2.1) is

$$\hat{\mathbf{L}} = -i\hbar \mathbf{r} \times \nabla. \quad (2.48)$$

The three components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ of this (vector) observable, given by Eqs. (2.40) and (2.41), do not commute. Indeed, after a simple calculation, one obtains

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y, \end{aligned} \quad (2.49)$$

which can be summarized as

$$\hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar \hat{\mathbf{L}}. \quad (2.50)$$

For systems of N particles with *position and momentum operators* $\hat{\mathbf{r}}_i, \hat{\mathbf{P}}_i$ with $i = 1, \dots, N$, the total angular momentum is

$$\hat{\mathbf{J}} = \sum_{i=1}^N \hat{\mathbf{L}}_i = \sum_{i=1}^N \hat{\mathbf{r}}_i \times \hat{\mathbf{P}}_i. \quad (2.51)$$

$\hat{\mathbf{J}}$ also satisfies the three commutation relations (Eq. (2.50)), which leads to take them as a definition of an *angular (vector) observable* $\hat{\mathbf{J}}$ with the following fundamental commutation relations between its components

$$\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar\hat{\mathbf{J}}. \quad (2.52)$$

The observable $\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$, which is associated to the square of the angular momentum, commutes with each component of $\hat{\mathbf{J}}$. Thus, the two operators $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ must have common eigenfunctions, denoted Ψ_{jm} , that obey the eigenvalue equations

$$\hat{\mathbf{J}}^2 \Psi_{jm} = j(j+1)\hbar^2 \Psi_{jm}, \quad (2.53)$$

and

$$\hat{J}_z \Psi_{jm} = m\hbar \Psi_{jm}, \quad (2.54)$$

with eigenvalues, $j(j+1)\hbar^2$ and $m\hbar$, respectively. j is called the *angular momentum quantum number* and m is called (for historical reasons) the *magnetic quantum number*. Let us also introduce the two operators

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y, \quad (2.55)$$

and

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y. \quad (2.56)$$

It can be shown that their action on Ψ_{jm} is

$$\hat{J}_+ \Psi_{jm} = \hbar\sqrt{j(j+1) - m(m+1)} \Psi_{j,m+1}, \quad (2.57)$$

and

$$\hat{J}_- \Psi_{jm} = \hbar\sqrt{j(j+1) - m(m-1)} \Psi_{j,m-1}. \quad (2.58)$$

For obvious reasons, $\hat{J}_+$ is called *raising operator* and $\hat{J}_-$ *lowering operator*. Through purely *algebraic* manipulations, Dirac was able to show the following quantization of j and m :

- j is a positive (or zero) integer or half integer:

$$j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots \quad (2.59)$$

- m is an integer or half integer, and for a given j , the only possible values of m are the $2j + 1$ numbers:

$$m = -j, -j + 1, \dots, j - 1, j. \quad (2.60)$$

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