



van Quantum tot Molecuul

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2 HC2: The quantum wave-function and Schroedinger equation

The Schroedinger equation, the quantum wave-function, the Born interpretation, mathematical tools of quantum mechanics, the free particle, Heisenberg's uncertainty principle.

Based on Atkins and de Paula, *Physical Chemistry*, 10th edition, Chapter 7.

In this lecture we present the mathematical framework of quantum theory, where the main entity is the *quantum wave-function*, and the dynamical equation that this wave-function must obey, the Schroedinger equation. We also introduce a number of mathematical tools which are required in the quantum formalism. We discuss Heisenberg's uncertainty principle, and show that it entails a fundamental limitation about the physical knowledge that we can have about quantum systems.

Learning goals of the lecture:

- (a) Understand that the state of a quantum system is described by the quantum wave-function, which is a solution of the Schroedinger equation.
- (b) Understand and apply the mathematical description of quantum physics, including hermitian operators, eigenvalue equations and orthogonality.
- (c) Understand how experimental observables can be calculated from the wave-function, and perform these calculations in simple systems.
- (d) Understand the Copenhagen interpretation of the physical meaning of the wave-function.
- (e) Understand and apply Heisenberg's uncertainty principle.

2.1 The quantum wave-function and Schroedinger's equation

The double slit experiment that we discussed in HC1 demonstrated the wave-like character of particles such as electrons. In quantum theory, the mathematical entity which is used to describe this and related phenomena is known as the *quantum wave-function* Ψ . More in general, the *complete physical properties of any quantum system* are uniquely determined once its wave-function Ψ is specified. The wave-function depends on the spatial and time coordinates of the N particles that constitute the quantum system,

$$\Psi = \Psi(x_1, y_1, z_1, t_1, \dots, x_N, y_N, z_N, t_N), \quad (2.1)$$

though in this course we will restrict ourselves to time-independent wave-functions.

The wave-function Ψ for a quantum system composed by a single particle satisfies the *Schroedinger equation*, which in one dimension x reads

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x) \quad (2.2)$$

where the various components of this equation are:

- m , the particle's mass.
- $V(x)$, the potential energy as a function of the position,
- E , the total energy of the system (which is a conserved quantity), and
- $\hbar \equiv h/2\pi$ is the *reduced Planck's constant*.

The Schroedinger equation is an *equation of motion* for quantum particles, playing a similar role that Newton's equation $F = ma$ has in classical mechanics.

The physical meaning of the wave-function can be interpreted as follows: if the wave-function of a particle takes the value $\Psi(x)$ for some point x , then $|\Psi(x)|^2 dx$ represents the *probability* that, upon performing a *measurement*, one will detect this particle in the region $[x, x + dx]$. In other words, $|\Psi(x)|^2$ represents the *probability density* in the coordinate x for this particle. Regions in x where $|\Psi(x)|^2$ is higher correspond to those regions where the particle has a higher likelihood to be found when a measurement is performed. This interpretation is known as the *Born interpretation of the wave-function*, and is illustrated in Fig. 1. Note that since in general the wave-function is a *complex function*, what is meant by “the square of the wave-function” has to be understood as

$$|\Psi|^2 = \Psi^*\Psi = [\text{Re}(\Psi) - i\text{Im}(\Psi)][\text{Re}(\Psi) + i\text{Im}(\Psi)], \quad (2.3)$$

and where the symbol $*$ stands for the complex conjugate operation.

Given that $|\Psi|^2$ is a probability density, it needs to be normalized appropriately. Since the probability of finding the particle *anywhere in space* must be unity, the wave-function must be normalized to ensure that

$$\int_{-\infty}^{\infty} dx |\Psi|^2(x) = 1. \quad (2.4)$$

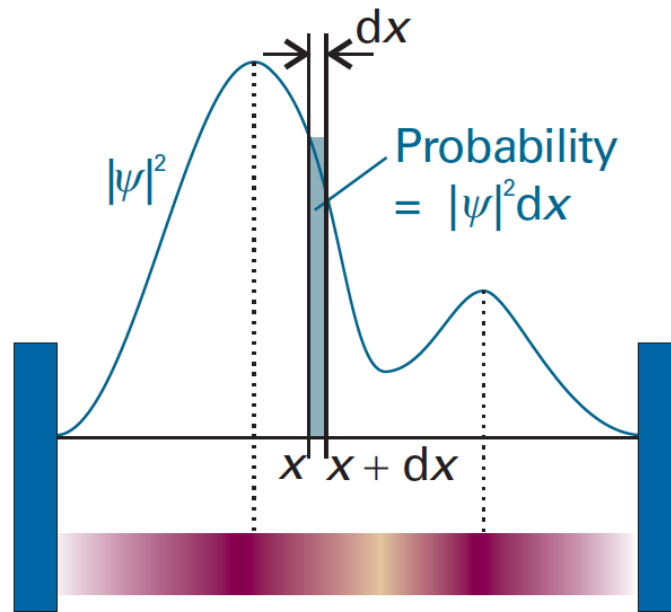


Figure 1: The physical interpretation of the quantum wave-function $\Psi(x)$ is that its square $|\Psi(x)|^2$ is the *probability density* associated to measuring the particle in a position x in space. Therefore, the *probability* to find the particle at position x in the range dx will be given by $|\Psi(x)|^2 dx$.

A wave-function $\tilde{\Psi}$ that does not satisfy this normalization condition can be rescaled by a constant factor $\Psi(x) = N \tilde{\Psi}$ given by

$$N = \left(\int_{-\infty}^{\infty} dx |\tilde{\Psi}|^2(x) \right)^{-1/2}, \quad (2.5)$$

so that the rescaled wave function Ψ satisfies the correct normalization requirement of Eq. (2.4).

The quantum wave-function Ψ needs to satisfy a number of important conditions everywhere in space:

- (a) it must be continuous,
- (b) its slope (first derivative) needs to be continuous as well,
- (c) it must be single-valued, and
- (d) it must be squared-integrable, Eq. (2.4), else the Born interpretation would lead to infinite (unphysical) probabilities.

As we will show now, for most physical systems these requirements imply that the energies that arise in the solution of the Schroedinger equation Eq. (2.2) can take only a finite set of values, that is, they lead to the *quantization of the energy*, which is one of the basic tenets of quantum theory.

2.2 The Schroedinger equation for a free particle

The simplest case that we can study with the Schroedinger equation is that of the motion of a *free particle*, that is, a particle which is not subjected to any form of potential, and thus has $V(x) = 0$. In this case the

Schroedinger equation Eq. (2.2) takes the following particular simple form:

$$-\frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E\Psi(x) \quad (2.6)$$

which is a second-order ordinary differential equation (ODE) that admits a solution in terms of a sum of exponentials (also known as *plane-wave* solutions):

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}, \quad (2.7)$$

where A and B are the *integration constants*, to be fixed by the initial conditions of the system, and the energy E and the *wave number* k are related by

$$E = \frac{\hbar^2 k^2}{2m}. \quad (2.8)$$

It is easy to show that $\Psi = Ae^{\pm ikx}$ is a solution of Eq. (2.6), since

$$-\frac{\hbar^2}{2m} \frac{d^2 Ae^{\pm ikx}}{dx^2} = -\frac{\hbar^2}{2m} (\pm ik)^2 Ae^{\pm ikx} = \frac{\hbar^2 k^2}{2m} Ae^{\pm ikx} = EAe^{\pm ikx}. \quad (2.9)$$

In general, rather than solving a Schroedinger equation from first principles, is also possible to assume a given solution and verify then if it is indeed a solution to this equation. Note that this system, E , the particle's kinetic energy, is *not quantized* and can take any value.

The solution of the free-particle Schroedinger's equation, Eq. (2.7), has the physical interpretation of the *superposition of two waves*, one moving in the positive and the other in the negative x direction - we will motivate more this interpretation below. For simplicity, let us set $B = 0$, and keep only the solution corresponding to a wave propagating in the positive x direction,

$$\Psi(x) = Ae^{ikx}. \quad (2.10)$$

At this point we can ask ourselves what is the *probability of finding the particle at a given point x in space*. Following Born's interpretation, the probability density for the position x of the particle will be given by the square of its wave-function,

$$|\Psi|^2 = (A^* e^{-ikx}) \cdot (A e^{ikx}) = |A|^2, \quad (2.11)$$

so we find the remarkable result that the particle has *exactly the same probability* of being found *anywhere in space*. In other words, its position is maximally undetermined. As we will show below, this indetermination is a direct consequence that we are assuming (unphysically) that the momentum $p = \sqrt{2mE} = \hbar k$ of the particle is known with infinite precision.

2.3 Eigenvalue equations in quantum theory

As we have mentioned above, the wave-function Ψ of a quantum system contains the complete physical information on a quantum system. In particular, the various properties of the system should be calculable from the knowledge of the wave-function. In quantum theory, we denote as an *observable* a given property of a quantum system (energy, momentum, angular momentum, electric charge, ...) that can be extracted

from a *measurement* of this system.

Mathematically, the tools that we will use to compute the expected outcome of a measurement of a quantum system are known as *operators*, which can be expressed in the language of *eigenfunctions* and *eigenvectors*. Formally, an *operator* is a way to represent the action of a specific mathematical function onto the wave-function Ψ . For instance, Schroedinger's equation Eq. (2.2) can be expressed in operator form as follows

$$\hat{H}\Psi(x) = E\Psi(x), \quad (2.12)$$

where the $\hat{}$ symbol indicates an operator, in this case the *Hamiltonian operator*, defined as

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \quad (2.13)$$

An equation of the form of Eq. (2.12) is known as an *eigenvalue equation*. In this case the application of the Hamiltonian operator to the wave-function returns the total energy E , since \hat{H} is the operator that represents the total energy of the quantum system.

In general, an eigenvalue equation will take the general form

$$\hat{\Omega}\Psi = \omega\Psi, \quad (2.14)$$

where:

- $\hat{\Omega}$ represents a generic operator associated to the observable property Ω ,
- Ψ is the *eigenfunction* this operator is acting upon, and
- ω is the eigenvalue of the operator $\hat{\Omega}$ associated with the eigenfunction Ψ .

Note that the eigenvalues ω are *constant numbers*, and cannot be functions of other variables. In general, eigenvalues will be complex numbers.

Let us try to become familiar with the concept of *eigenvalue equation* with a couple of examples:

- (a) Is $\Psi(x) = e^{\alpha x}$ an eigenfunction of the operator $\hat{\Omega} \equiv d/dx$? To verify if this is the case, we apply the operator to the wave-function to find

$$\hat{\Omega}\Psi = \frac{d}{dx}e^{\alpha x} = \alpha e^{\alpha x} = \alpha\Psi, \quad (2.15)$$

so indeed in this case $\Psi(x)$ is an eigenfunction, with α being the associated eigenvalue.

- (b) Is $\Psi(x) = e^{\alpha x^2}$ an eigenfunction of the same operator? Let us check it in the same way as before:

$$\hat{\Omega}\Psi = \frac{d}{dx}e^{\alpha x^2} = (2\alpha x)e^{\alpha x^2} = 2\alpha x\Psi \neq \omega\Psi, \quad (2.16)$$

thus now Ψ is *not* an eigenfunction, since it would have a non-constant eigenvalue, and this is not allowed.

As mentioned above, the Schroedinger equation itself is an eigenvalue equation, Eq. (2.12). For each state with a definite energy (eigenvalue) E , there corresponds a unique wave-function Ψ (the eigenfunction).

Note that in general the Schroedinger equation Eq. (2.12) will admit different solutions for the wave-function Ψ_n , each with their associated energy E_n , where by n we indicate a general quantum number which is used to label the solutions of the eigensystem.

2.4 Operators and physical observables

In quantum theory, the eigenvalues of specific operators such as the Hamiltonian \hat{H} correspond to *observables* of the system, in this case the total energy. Indeed, *each observable* of a quantum system, such as position, momentum, or angular momentum of the constituent particles, will have *associated an operator* that, when acting on the wave-function, will return the corresponding physical property as the eigenvalue. We now discuss this property in more detail.

In quantum mechanics, any *observable property* Ω of the quantum system will be represented by an operator $\hat{\Omega}$ built up from the *position* and *momentum* operators, defined respectively as

$$\hat{x} \equiv x, \quad (2.17)$$

$$\hat{p}_x \equiv \frac{\hbar}{i} \frac{d}{dx}. \quad (2.18)$$

For example, let us consider the free-particle solution of Schroedinger's equation, Eq. (2.7), and compute what happens if we apply to it the momentum operator \hat{p} . Setting $B = 0$ first, we get that

$$\hat{p}\Psi(x) = \left(\frac{\hbar}{i} \frac{d}{dx}\right) A e^{ikx} = \hbar k A e^{ikx} = \hbar k \Psi(x), \quad (2.19)$$

so the momentum along the x direction p_x that can be associated to the free particle is $p_x = +\hbar k$. This is consistent with the fact that for a given value of k , the kinetic energy is $E = \hbar^2 k^2 / 2m$ and thus $p = \sqrt{2mE} = \hbar k$. It can similarly be shown that the $A = 0$ solution has associated momentum $p_x = -\hbar k$. Therefore, the case $B = 0$ corresponds to a particle moving in the positive x direction with momentum $p_x = +\hbar k$. This calculation indicates that the free-particle solutions of Schroedinger's equation are *eigenfunctions of the momentum operator* in addition to of the Hamiltonian, that is, they represent solutions with well-defined momentum.

Similar considerations apply to other examples. First, the potential energy operator in the case of an harmonic-like potential (such as that for an harmonic oscillator) will be represented by the operator

$$\hat{V} = V(x) = \frac{1}{2} k x^2, \quad (2.20)$$

which is representative of the simplest type of operators, those whose effect correspond to multiply Ψ by a function (as compared to more complex manipulations like taking derivatives). For the kinetic energy, $E_k = mv^2/2 = p^2/2m$, the corresponding operator can be constructed from the momentum operator

$$\hat{E}_k = \frac{1}{2m} (\hat{p})^2 = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx}\right) \left(\frac{\hbar}{i} \frac{d}{dx}\right) = -\frac{\hbar}{2m} \frac{d^2}{dx^2}. \quad (2.21)$$

Of course, the combination of the kinetic energy and the potential energy operators corresponds to the

Hamiltonian operator, whose eigenvalue is the total energy of the system

$$\hat{H} = \hat{E}_k + \hat{V} = -\frac{\hbar}{2m} \frac{d^2}{dx^2} + \hat{V}. \quad (2.22)$$

Before continuing, it is important to consider the mathematical properties that operators must satisfy in order to represent observables of a quantum system.

2.5 Hermitian operators and orthogonality

We have just mentioned that, in quantum mechanics, observable properties of a system have associated operators, whose eigenvalues correspond to the values than these observables can take when the measurement is performed. However, not all operators will lead to physically sensible observables. In particular, only operators which are *Hermitian* are physically allowed. Hermitian operators have important properties, such as they always lead to real (as opposed to complex) eigenvalues, and that the eigenfunctions of Hermitian operators are *orthogonal* among them.

An Hermitian operator $\hat{\Omega}$ is such that, given two arbitrary wave-functions Ψ_i and Ψ_j , it satisfies the following property:

$$\int dx \Psi_i^* \hat{\Omega} \Psi_j = \left(\int dx \Psi_j^* \hat{\Omega} \Psi_i \right)^\dagger. \quad (2.23)$$

It is easy to check that both the momentum and position operators \hat{x} and \hat{p} are Hermitian. For instance, in the case of \hat{p} we have

$$\int dx \Psi_i^* \hat{p} \Psi_j = \int dx \Psi_i^* \frac{\hbar}{i} \frac{d}{dx} \Psi_j = \frac{\hbar}{i} \left(\Psi_i^* \Psi_j \Big|_{-\infty}^{+\infty} - \int dx \Psi_j \frac{d}{dx} \Psi_i^* \right) = - \int dx \Psi_j \frac{\hbar}{i} \frac{d}{dx} \Psi_i^* \quad (2.24)$$

where we have used integration by parts, and exploited the facts that wave-functions must vanish at infinity. Noting that the \dagger in Eq. (2.23) indicates that the operator now acts to its left, then we have demonstrated that \hat{p} is Hermitian. In quantum theory, all observables are indeed represented by Hermitian operators, ensuring that the expectation values of these observables in physical systems are real (a system cannot have *i.e.* complex energy).

This key property that the eigenvalues of an Hermitian operator $\hat{\Omega}$ are real can be demonstrated from its definition Eq. (2.23) as follows. Let us assume that $\Psi_i = \Psi_j = \psi$ is an eigenfunction of this operator with eigenvalue ω , that is $\hat{\Omega}\psi = \omega\psi$. Then we have that

$$\int dx \psi^* \hat{\Omega} \psi = \int dx \psi^* \omega \psi = \omega \int dx \psi^* \psi = \omega, \quad (2.25)$$

since the wave-function is normalized to one, and that also we have that the conjugate of the above expression gives

$$\left(\int dx \psi^* \hat{\Omega} \psi \right)^\dagger = \left(\omega \int dx \psi^\dagger \psi \right)^* = \omega^* \quad (2.26)$$

and since $\hat{\Omega}$ is hermitian, then $\omega^* = \omega$, that is, ω is a real number.

It is also possible to show that, for an hermitian operator, its eigenfunctions are *orthogonal* among them. In other words, they constitute a *set of linearly independent basis functions*. Mathematically, the

orthogonality property implies that

$$\int dx \Psi_i^*(x) \Psi_j(x) = \delta_{ij}, \quad (2.27)$$

that is, the integral vanishes unless the eigenfunctions are the same, $i = j$, in which case the integral equals one because of the normalization condition. This important property allows to express a general quantum state as a *linear superposition* of eigenfunctions of an Hermitian operator.

2.6 Quantum superposition and expectation values

The wave-function Ψ can be used to determine the *expectation value* of physical observables of a quantum system. In general, there will be multiple solutions Ψ_n of the Schroedinger equation, each of them being a specific eigenfunction of the Hamiltonian and thus characterized by well-defined energies E_n . Since Schroedinger's equation is a *linear* differential equation, it exhibits the property that the *superposition* of N independent solutions,

$$\tilde{\Psi} \equiv \sum_{n=1}^N \Psi_n \quad (2.28)$$

is itself *also be a solution* of the same equation. On the other hand, the new solution Eq. (2.28) will in general *not be an eigenfunction* of the Hamiltonian operator \hat{H} , and thus will not have associated a well-defined energy E . Indeed, if we apply the Hamiltonian operator to Eq. (2.28) we find that

$$\hat{H}\tilde{\Psi} = \sum_{n=1}^N \hat{H}\Psi_n = \sum_{n=1}^N E_n \Psi_n \neq E\tilde{\Psi}. \quad (2.29)$$

Therefore, while a superposition of eigenfunctions constitutes a valid solution of the original Schroedinger equation, it is not an eigenfunction itself. Crucially, in the limit $N \rightarrow \infty$ the basis provided by the $\{\Psi_n\}$ eigenfunctions of an Hermitian operator is *complete*, that is, any arbitrary function can be expressed as a linear combination of the elements of the $\{\Psi_n\}$ basis.

An explicit example of the fact that a superposition of eigenfunctions of a given Hermitian operator is not necessarily an eigenfunction itself is provided by the free particle solution, Eq. (2.7) in the case that we set $B = A$. In this case, the wave-function can be written as

$$\Psi = A(e^{ikx} + e^{-ikx}) = 2A \cos(kx), \quad (2.30)$$

which as shown above corresponds to the superposition of one plane wave moving to the right with momentum $p_x = +\hbar k$ and another one moving to the left with $p_x = -\hbar k$. If now we apply the momentum operator to this wave-function, we find

$$\hat{p}_x \Psi = \frac{\hbar}{i} \frac{d\Psi}{dx} = -\frac{2k\hbar}{i} A \sin(kx) \neq p_x \Psi, \quad (2.31)$$

therefore showing that the superposition of two wave-functions with well-defined momentum p_x is not itself an eigenfunction of this same operator, and therefore does not have a well-defined momentum. Note that, on the other hand, the solution Eq. (2.30) *is* of course an eigenvalue of the Hamiltonian operator, since

$$\hat{H}\Psi = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} 2A \cos(kx) = \frac{\hbar^2}{2m} 2Ak^2 \cos(kx) = \frac{\hbar^2 k^2}{2m} \Psi = E\Psi, \quad (2.32)$$

with the eigenvalue being the total energy of the system, as expected from the linear property of \hat{H} .

The example above demonstrate that eigenfunctions of the Hamiltonian operator, that is, the solutions of the Schrodinger equation, are not necessarily eigenfunctions of other Hermitian operators. Therefore, how it is possible to determine the expectation values for generic observables of quantum states?

To answer this question, let us start by assuming that we have a quantum state such as Eq. (2.30). In this system, each measurement of the momentum of the particle will return either $+k\hbar$ or $-k\hbar$ with equal probability. Therefore the *expectation value* for the operator \hat{p}_x for the quantum state Eq. (2.30) will be given by

$$\langle p_x \rangle = \frac{1}{2} \cdot (+k\hbar) + \frac{1}{2} \cdot (-k\hbar) = 0, \quad (2.33)$$

where we have weighted each eigenvalue by its probability. Therefore, while individual measurements will always return one of the two possible values of the momentum, either $+k\hbar$ or $-k\hbar$, the average value over many measurements will vanish.

More in general, if we express a given wave-function as a linear superposition of eigenfunctions of an Hermitian operator $\hat{\Omega}$, which we can always do since these eigenfunctions form a complete basis, we have

$$\Psi = \sum_k c_k \Psi_k, \quad \hat{\Omega}\Psi_k = \omega_k \Psi_k, \quad (2.34)$$

and then the probability that a given measurement of the physical observable Ω will yield ω_k will be

$$P(\omega_k) = \frac{c_k^2}{\sum_j c_j^2}. \quad (2.35)$$

Therefore, the expectation value of the observable Ω (that is, the average over a large number of measurements) will then be given by

$$\langle \Omega \rangle = \sum_k \left(\frac{c_k^2}{\sum_j c_j^2} \right) \omega_k, \quad (2.36)$$

where each possible value of that the observable Ω can take in this quantum system (*i. e.* each possible eigenvalue) is weighted by its associated probability.

An equivalent way of computing the expectation value of the observable Ω in terms of the wave-function is given by the following expression:

$$\langle \Omega \rangle = \int dx \Psi^* \hat{\Omega} \Psi, \quad (2.37)$$

which can be shown to be equivalent to above. Moreover, it is also easy to show that, using the definition Eq. (2.37) the expectation value of an Hermitian operator $\hat{\Omega}$ for a quantum state where the wave function is an eigenfunction Ψ of this operator is nothing but the eigenvalue ω . Indeed one has

$$\langle \Omega \rangle = \int dx \Psi^* \hat{\Omega} \Psi = \int dx \Psi^* \omega \Psi = \omega \int dx \Psi^* \Psi = \omega, \quad (2.38)$$

due to the normalization of the wave-function.

Thus if a quantum state Ψ is not an eigenfunction of $\hat{\Omega}$, but rather a linear combination of its eigenfunctions Ψ_k each with eigenvalue ω_k ,

$$\Psi = \sum_k c_k \Psi_k, \quad (2.39)$$

then the expectation value will be given by the weighted sum of eigenvalues, with weight $|c_k|^2$:

$$\langle \Omega \rangle = \int dx \left(\sum_k c_k \Psi_k \right)^* \hat{\Omega} \left(\sum_j c_j \Psi_j \right) = \sum_{k,j} c_k^* c_j \omega_j \int dx \Psi_k^* \Psi_j = \sum_{k,j} c_k^* c_j \omega_j \delta_{ij} = \sum_k |c_k|^2 \omega_k, \quad (2.40)$$

where we have use the orthogonality property of the eigenfunctions of an Hermitian operator, namely Eq. (2.27). Note that in this derivation we assume that the coefficients of the linear superposition Eq. (2.47) are canonically normalized, that is, they satisfy

$$\sum_k |c_k|^2 = 1, \quad (2.41)$$

which physically means that the probability of finding the quantum state Ψ in any of the eigenfunction Φ_k is simply unity (conservation of probability).

2.7 Heisenberg's uncertainty principle

Let us now go back to the free-particle solution of Schroedinger's equation for a plane wave propagating in the positive x direction,

$$\Psi = Ae^{ikx}, \quad (2.42)$$

where we found that the probability distribution for the position of the particle was $|\Psi|^2 = A^2$, namely flat: the position of a free particle is maximally undetermined. We also found that, on the other hand, the momentum of this free particle $\hat{p}_x \Psi = (\hbar/i)(d/dx)\Psi = p_x \Psi$ was $+k\hbar$, a well defined value. So why for a free particle we have *maximum uncertainty concerning its position* but instead *perfect information concerning its momentum*?

The reason for this is another of the central principles of quantum mechanics, *Heisenberg's uncertainty principle*. This principle states that *it is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle*. Note that this is not a mere practical limitation due to for example the finite resolution of our measurement apparatus, but a *fundamental limitation* of the theory that holds true even in the case of ideal measurements. Mathematically, Heisenberg's uncertainty principle takes the following form:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}, \quad (2.43)$$

or in other words, the better the position of a particle is known, the greater the uncertainty concerning its momentum will be. This explains the expectation values of \hat{x} and \hat{p} in the case of a free particle: since the uncertainty on its momentum its zero ($p = \hbar k$) then the uncertainty on its position, due to Eq. (2.43), must be *infinite*, and indeed the probability distribution for the position of the free particle is the same everywhere in space.

Mathematically, the uncertainty in the two observables, x and p , is computed from the square root of the *variance*, known as the *standard deviation*, of the distribution of values that these two operators can take, that is

$$\Delta x \equiv \left(\langle x^2 \rangle - \langle x \rangle^2 \right)^{1/2}, \quad (2.44)$$

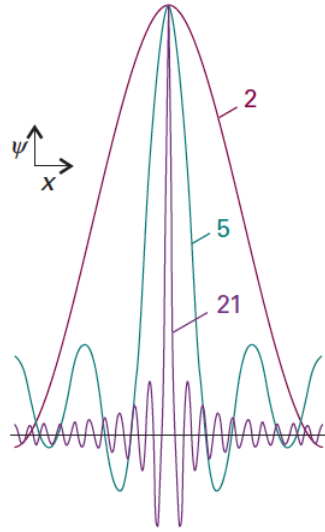


Figure 2: The wave function Eq. (2.47) corresponding to the superposition of N plane-wave free particle solutions, each with a different value of $k = n\pi$. We show the results from the addition of $N = 2, 5, 21$ terms in Eq. (2.47), showing that the more terms we include, the better the localization of the free particle (since the higher is the indetermination of its momentum p_x).

$$\Delta p \equiv \left(\langle p^2 \rangle - \langle p \rangle^2 \right)^{1/2}, \quad (2.45)$$

where $\langle x^2 \rangle$ stands for the expectation value of the \hat{x}^2 operator and so on.

Does this imply that the position of a free particle is always maximally uncertainty? No, if we take into account that physically, from Eq. (2.43), there should be an uncertainty associated also to the expectation value of \hat{p} , the momentum of the quantum state. A wave function for a free particle with a *finite momentum resolution* can be achieved by constructing a *superposition* of free-particle solutions, each with *different wave numbers* k , namely

$$\Psi(x) = \sum_k^N c_k e^{ikx}. \quad (2.46)$$

The more the number of contributions N to the above sum, the higher the uncertainty on the momentum of the particle, and thus we obtain an increased localization of the particle in x . This can be seen by plotting the free-particle wave-function superposition:

$$\Psi(x) = \sum_{n=1}^N \cos(n\pi x), \quad (2.47)$$

which is shown in Fig. 2: the more terms we add in the sum, the more values the momentum $\hbar k$ of the particle can take, hence Δp is higher (more uncertain) and Δx smaller (increased localization in space).

To be more precise about Eq. (2.43), there are two important remarks to be done. First of all, Heisenberg's uncertainty principle applies only to position and momentum *along the same spatial direction*. So actually we have

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}, \quad \Delta y \Delta p_y \geq \frac{\hbar}{2}, \quad \Delta z \Delta p_z \geq \frac{\hbar}{2}, \quad (2.48)$$

but on the other hand we can also have for instance $\Delta x \Delta p_y = 0$, that is, it is possible to *simultaneously*

measure x and p_x with arbitrary precision.

The second important implication of Heisenberg's uncertainty principle is that it illustrates a more general concept of quantum theory known as *complementary observables*. We define two observables Ω_1 and Ω_2 to be *complementary* if the sequential application of the corresponding operators $\hat{\Omega}_1$ and $\hat{\Omega}_2$ does not *commute*, that is,

$$\hat{\Omega}_1 (\hat{\Omega}_2 \Psi) \neq \hat{\Omega}_2 (\hat{\Omega}_1 \Psi), \quad (2.49)$$

or in other words, the results of applying the two operators $\hat{\Omega}_1$ and $\hat{\Omega}_2$ to a generic wave-function depends on the *order in which they have been applied*. It can be demonstrated that for each pair of complementary observables there will be a relation of the form of Eq. (2.43), implying that a simultaneous measurement of Ω_1 and Ω_2 with arbitrary precision is not possible.

The result that in quantum theory the subsequent application of Hermitian operators to a quantum system does not necessarily commute can be represented introducing another useful mathematical concept, the *commutator* between two operators, defined as

$$[\hat{\Omega}_1, \hat{\Omega}_2] \equiv \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1, \quad (2.50)$$

where note that the commutator of two operators *is another operator*, that is, it should be understood as being applied to a wave-function. With this definition, for the position and momentum operators we find

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad (2.51)$$

as is easy to verify explicitly. Indeed, since

$$\hat{x} \hat{p}_x \Psi = x \left(\frac{\hbar}{i} \frac{d}{dx} \right) \Psi = \frac{\hbar}{i} x \frac{d\Psi}{dx}, \quad (2.52)$$

$$\hat{p}_x \hat{x} \Psi = \left(\frac{\hbar}{i} \frac{d}{dx} \right) (x\Psi) = \frac{\hbar}{i} \Psi + \frac{\hbar}{i} x \frac{d\Psi}{dx}, \quad (2.53)$$

then their commutator gives

$$[\hat{x}, \hat{p}_x] \Psi = -\frac{\hbar}{i} \Psi = i\hbar \Psi, \quad (2.54)$$

which is the sought-for result Eq. (2.51). Therefore, x and p are *complementary observables* (their operators do not commute) and thus they cannot be measured simultaneously with arbitrary precision. This is another way of representing Heisenberg's uncertainty principle.

2.8 Overview of the postulates of quantum theory

We can now recapitulate what we have learned in this lecture about the *basic postulates of quantum mechanics*. These are fundamental assumptions, not derived from any other theory (at least so far), and play a similar role as the axioms of a mathematical system. These postulates are:

- (a) All the physical information about a quantum system is contained in its *wave-function* Ψ .
- (b) This wave-function satisfies a specific equation of motion, known as the *Schroedinger equation*.