

Wavefunctions

In quantum mechanics (QM) the state of a particle is not described by actual values of dynamics variables (such as position and momentum) but, rather, by a probability distribution, which tells us what is the probability of finding a particle in a specific position. For instance, the probability of finding the particle in an interval $[r, r + dr]$ is given by $P(r, r + dr) = F(r)dr$. The particle wavefunction is defined such that its modulus square equals the probability distribution $F(r)$, so that the probability can be written as:

$$P(r, r + dr) = |\psi(r)|^2 dr \quad (1)$$

As such, a fundamental property of a wavefunction is that it is normalised. Physically, this means that the probability of finding a particle anywhere in space must be 100%. This implies that:

$$\int_{-\infty}^{+\infty} |\psi(r)|^2 dr = 1 \quad (2)$$

More generally, the class of functions such that $\int_{-\infty}^{+\infty} |\psi(r)|^2 dr < \infty$ is called the Hilbert space and is generally denoted as L^2 . For examples, e^{-x^2} belongs to the Hilbert space, e^{-x} does not (try to demonstrate it).

The Hilbert space is a vectorial space, i.e., it behaves exactly in the same way has the usual vectorial space in x, y, z that you are used to. As such, one can define a scalar product, that in QM is defined as: $\langle \psi | \phi \rangle \equiv \int_{-\infty}^{+\infty} \psi^* \phi dr = c$. c here is, generally speaking, a complex number. If two wavefunctions are independent from each other, or orthogonal, then their scalar product is zero.

Operators

What about the description of other dynamic variables? In QM, each dynamic variable is described by an operator. In essence, this comes from the empirical observation that the physical act of measuring a quantity does interfere with the system being measured and thus modifies the state of the system. Let us assume you want to measure the momentum p of a particle in a state described by the wavefunction ψ . After the measurement, the system will be perturbed, and thus described by a new wavefunction ϕ . Formally, this is stated by saying that the momentum is described by an operator \hat{P} , such that: $\hat{P}(\psi(r)) = \phi(r)$.

Operators are thus functions that work on the Hilbert space.

But about the result of this measurement? Generally, QM does not allow one to predict the exact outcome of a measurement (classical mechanics would) but it can only predict the probability that a certain value would be obtained. Only in specific cases, the result will be uniquely defined, i.e., if the physical system is described by an eigenfunction of the operator. If an operator is applied onto one of its eigenfunctions, the result would be the eigenfunction itself multiplied by a constant. That is to say that, if ψ is an eigenfunction of \hat{P} , $\hat{P}(\psi(r)) = \lambda\psi(r)$. λ , which is in general a complex number, is called the eigenvalue of ψ . It is important to note that bound systems (spatially confined) are always quantised, meaning that the eigenvalues can only get discrete values.

In general though, the state of the system will not be an eigenfunction of the operator. However, one can demonstrate that any physical state can be expressed as a combination of eigenfunctions. Let us assume that we want to measure the momentum (modelled by the operator \hat{P}) of a system described by the wavefunction ϕ . We also assume that we know all the eigenfunctions of \hat{P} , and we call them ψ_i . This is to say that we know all the functions that, when \hat{P} is applied to them, return the same wavefunction times a constant: $\hat{P}(\psi_i(r)) = \lambda_i\psi_i(r)$. It can be demonstrated that the wavefunction of the system ϕ can always be expressed as a combination of the ψ_i : $\phi = \sum_i c_i\psi_i$. Importantly, all eigenfunctions are orthogonal to each other.

When trying to measure the momentum on the system described by ϕ , one can obtain any of the eigenvalues of \hat{P} (i.e., any λ_i), each with a probability $|c_i|^2$. An important quantity is the average value, i.e., what one would measure on average. Let's call the average value $\bar{\lambda}$, which is given by: $\bar{\lambda} = \sum |c_i|^2 \lambda_i$ or, equivalently, by $\langle \phi | \hat{P} | \phi \rangle \equiv \int_{-\infty}^{+\infty} \phi^* \hat{P} \phi dr$ (try to demonstrate that). An important property of the mean value is that this would be the result of the measurement in classical mechanics. In other words, classical mechanics is the physics of the mean values of a system.

Obviously, not all operators are associated with a dynamic variable (or, observable). One important requisite is that all eigenvalues of an operator must be real numbers. This is because eigenvalues are possible results of a measurement and it is impossible to directly measure a complex number. Operators that have all real eigenvalues are called hermitian. In other words a dynamic variable can only be associated to a hermitian operator. Equivalently, an operator \hat{A} is hermitian if it is equal to its transpose complex conjugated, i.e., if $(\hat{A}^\dagger)^* = \hat{A}$.

Finally, the result of measuring two different quantities (such as position and momentum) might depend on the order these two operations are performed. For example measuring first the position and then the momentum of a particle gives a different result than measuring the momentum first and then the position. This is equivalent to say that $\hat{P}(\hat{r}(\psi)) \neq \hat{r}(\hat{P}(\psi))$. In QM, this is expressed by saying that the commutator between these two operators is non-zero. For instance, in the case of position and momentum, this is expressed as: $[\hat{r}, \hat{P}] \equiv \hat{r}\hat{P} - \hat{P}\hat{r} = i\hbar$.

An important property of the commutator is that, if two operators commute, then they share the same eigenfunctions (but not eigenvalues!) and can be measured simultaneously with infinite precision. On the other hand, if two operators do not commute, then they will have an associated uncertainty principle. In the example of position and momentum:

$$\Delta r \Delta P \equiv \frac{|[\hat{r}, \hat{P}]|}{2} = \hbar/2 \quad (3)$$

Temporal evolution

Operators can be used to describe the systems at rest. The temporal evolution of a system is instead described by the Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t} \psi(r, t) = \hat{H}\psi(r, t) \quad (4)$$

where \hat{H} is the hamiltonian of the system, sum of the operator potential energy \hat{V} and operator kinetic energy \hat{T} . Similarly to classical mechanics, $\hat{T} = \hat{P}^2/2m$, with the only difference that in QM the operator momentum is defined as $\hat{P} = -i\hbar\nabla$. The time-independent variant of the Schrodinger equation (is the time-independent)i.e., the system is static, is $\hat{H}\psi_i = E_i\psi_i$. Here, E_i are real numbers and represent the eigenvalues of the energy. In other words, solving the time-independent Schrodinger equation gives the energy states of the system ψ_i and the energy levels E_i . As examples, we have seen the energy levels of a potential well and of the harmonic oscillator. For the latter we have also seen ladder operators (creation and annihilation) and how this leads to analogies with the electromagnetic field. We have seen that the temporal evolution of the mean value of the operator is described by the Ehrenfest theorem, which also explains the dynamic equations of classical mechanics as the equations of mean values in QM.

Angular Momentum

Particularly complicated operators in QM are those describing the angular momentum. In

QM, there are three main angular momenta: the orbital angular momentum \hat{L} , the spin \hat{S} and the total angular momentum $\hat{J} = \hat{L} + \hat{S}$. Any property obtained for one of them strictly applies to any other. The main difference with classical mechanics is the presence of the spin, which is an intrinsic property of any particle and does not have any classical counterpart whatsoever. Unfortunately, different components of the angular momentum do not commute with each other, but they only commute with the total angular momentum. In other words, one can only measure simultaneously the total angular momentum and one of its components, e.g., $[\hat{L}^2, \hat{L}_x] = 0$ but $[\hat{L}_y, \hat{L}_x] \neq 0$. Another property is that the angular momentum is always quantised.

We can express the eigenvalues of \hat{L}^2 as $\ell(\ell+1)\hbar$, where ℓ can only be an integer or half integer number. Generally, when discussing the angular momentum, \hbar is omitted (i.e., units are used so that \hbar is equal to 1). If that is the case, the possible eigenvalues of one component of the angular momentum can only be between ℓ and $-\ell$ in steps of 1, i.e., $-\ell \leq m \leq \ell$. The eigenfunctions of the orbital angular momentum are the spherical harmonics $Y_{\ell,m}(\theta, \phi)$, parametrised by ℓ and m :

$$\hat{L}^2 Y_{\ell,m}(\theta, \phi) = \ell(\ell+1) Y_{\ell,m}(\theta, \phi) \quad , \quad \hat{L}_3 Y_{\ell,m}(\theta, \phi) = m Y_{\ell,m}(\theta, \phi) \quad (5)$$

The two relations above are valid simultaneously. This brings in degeneracy of the system, since different values of m can be associated with the same ℓ . In this case the degeneracy is $\text{DEG} = 2\ell + 1$. For example, a particle with $\ell = 2$ can have 5 different values of $m = -2, -1, 0, 1, 2$.

When summing spin and orbital angular momentum, one obtains the total angular momentum of the particle j . Here, one must be careful, because the relations given above imply that j is not simply the sum of ℓ and s but, rather, any value between $\ell + s$ and $\ell - s$ in steps of 1. This also implies that the total degeneracy of the angular momentum is $(2\ell + 1)(2s + 1)$. For example, a particle with $\ell = 2$ and $s = 1/2$ has a total degeneracy of $(2\ell + 1)(2s + 1) = 10$ and the possible values of j are $\ell + s = 5/2$ and $\ell - s = 3/2$. So, for this example: $\ell = 2$, $m = -2, -1, 0, 1, 2$ (degeneracy of 5), $s = 1/2$, $s_z = -1/2, 1/2$ (degeneracy of 2), $j = 5/2, 3/2$, $j_z = -5/2, -3/2, -1/2, 1/2, 3/2, 5/2$ (degeneracy of 10). Numbers from $-3/2$ to $3/2$ are repeated twice (double-degenerate) because they corresponds to different states.

We have seen that particles with half integer spin are called fermions and particles with

integer spin are called bosons. These two classes of particles have completely different behaviour. For instance, the Pauli exclusion principle only applies to fermions.

From these considerations, we have arrived at writing the full equation for the hydrogen atom, and the four magic numbers describing the state of an electron in an atom.

Perturbation theory

Generally, solving the Schrodinger equation is challenging, since it is a second-order non-linear partial differential equation. Some approximations can be adopted to ease calculations. For instance, we have seen the case of a system at rest, described by the hamiltonian \hat{H}_0 , which is perturbed by a small external influence, described by the perturbation hamiltonian \hat{H}' . The assumption is that all eigenfunctions and eigenvalues of \hat{H}_0 are already known and we want to find how they get modified when \hat{H}' is introduced. We have seen two main cases: \hat{H}' dependent or independent of time.

For time-independent perturbations, the system is not allowed to transition from one state to another but the actual energy levels are slightly modified, i.e., they go from E_0 (eigenvalues of \hat{H}_0) to $E_1 = E_0 + E'$ (eigenvalues of $\hat{H} = \hat{H}_0 + \hat{H}'$). Since we assume that E_0 is known, we just need to find E' . If a perturbation approach can be used, E' is only the mean value of \hat{H}' , i.e.:

$$E' \approx \langle \psi | \hat{H}' | \psi \rangle \quad (6)$$

Once E' has been calculated it is always good to check that the perturbation approach holds, i.e., one has to check that $E' \ll E_0$.

If the perturbation depends on time, the situation is more complicated, since now the system has a finite probability of jumping from one state to the other. In the notes, you have the expression for the transition probability. One important class of transition is the adiabatic transitions, i.e., perturbations that happen so slowly in time that the system does not jump, regardless of the strength of the perturbation. The condition for this to happen is given in Eq. 15 of lecture 20.

In the solved problems lecture (lecture 21) you have practical examples of this works.