Quantum Mechanics I

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Contents

Probability Functions

Quantum mechanics is based on the study of the wave function. The wave function is a semi-abstract thing whose magnitude is a probability function. Thus the study of quantum mechanics begins with some study of probability.

1.1 WEIGHTED FUNCTIONS

When considering a discrete system the **expected value** is the hypothetical mean result if you were to take many measurements of a system.

If you have a discrete, normalized weighted function and some other function, in this case x, the average of the other function is found by

$$\langle x \rangle = \sum_{i=1}^{n} = w_i \, x_i \tag{1}$$

For continuous functions individual weights are replaced with a **probability distribution function**:

$$\langle x \rangle = \int x \, \rho(x) \, dx \tag{2}$$

$$\text{Normal} \equiv \int \rho(x) \, dx = 1 \tag{3}$$

w_i has been generalized to a **probability distribution function, $\rho(x)$**, which is unitless.

1.1.1 Variance and standard deviation

$$\text{Variance} \equiv \sigma^2 = \langle s^2 \rangle - \langle s \rangle^2 = \langle (\Delta s)^2 \rangle = \langle (x - \langle x \rangle)^2 \rangle \tag{4}$$

$$\sigma \equiv \text{standard deviation.}$$

1.2 PROPERTIES OF QUANTUM WEIGHTED DISTRIBUTIONS

$$\langle a \rangle = \int \hat{a} \, |\Psi(a)|^2 \, dx = \int \Psi^* \hat{a} \Psi \, dx \tag{5}$$

Gives the expected value a. It is integrated over space. $|\Psi(x)|$ is experimentally measured, given, or derived.

Here $\hat{a}$ is an operator, Ψ is the wave function, and $|\Psi|^2$ is the probability function.

An important property of quantum functions is that they must satisfy these edge requirements:

$$\Psi(\text{edge}) = 0, \text{ and, } \Psi'(\text{edge}) = 0 \qquad (6)$$

1.2.1 Derivatives of Expected Values

The derivative of an expected value gives the expected value of that… as in

$$\langle p \rangle = m \langle \frac{dx}{dt} \rangle = m \frac{d\langle x \rangle}{dt} \qquad (7)$$

2

Schrodinger Equation

First, the full Equation

$$ i\hbar \frac{d\Psi}{dt}(r,t) = \frac{-\hbar^2}{2m} \nabla^2 \Psi(r,t) + V(r)\Psi(r,t) \tag{8} $$

First we assume the Schrodinger equation is time independent, then solve for a potential $V(x,t)$, although we are assuming that V is actually time independent.

This becomes the following, known as the **time- independent Schrodinger Equation**.

$$ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \tag{9} $$

This system can be solved for different potential function, $V(x)$, often using separation of variables, at least the infinite square well and harmonic operator.

The time-independent equation can also be written

$$ \hat{H}\Psi = E\Psi \tag{10} $$

which holds for any component of the total solution as well.

2.1 BUILDING THE FULL SOLUTION, TIME-DEPENDENCE

Any wave function can be fully represented by a solution of the following form

$$ \Psi(x,t) = \sum c_n \psi_n(x) e^{-\frac{iE_n t}{\hbar}} \tag{11} $$

These problems begin with a defined (measurable) $\Psi(x,0)$. The general solution to the coefficients, c_n is as follows

$$ c_n = \int \psi_n^* \Psi(x,0) dx \tag{12} $$

These coefficients correspond to the probability of measuring different energy levels. The sum of all should be 1.

$$ |c_n|^2 = 1 \tag{13} $$

The expectation value of the energy is then

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n \tag{14}$$

A is found by normalizing $|\Psi(x,0)|^2$,

$$1 = A^2 \int |\Psi(x,0)|^2 dx \tag{15}$$

Each component of the total solution (each ψ in Ψ) is orthogonal and normalized:

$$\int \psi_m(x)^* \psi_n(x) dx = \delta_{mn} \tag{16}$$

Solutions of the Schrodinger Equation

3.1 THE INFINITE SQUARE WELL

let

$$V(X) = \begin{cases} 0 & 0 < x < a \\ \infty & \text{else} \end{cases}.$$

Using this with the time-independent Schrodinger equation yields

$$\hat{H}\Psi = -\frac{\hbar^2}{2m}\Psi'' = E\Psi \tag{17}$$

Which is in the form of the common wave equation differential equation, and yields the following solutions.

$$\psi_n = \sqrt{\frac{2}{a}}\sin(\frac{n\pi}{a}x), \quad E_n = \frac{\hbar^2\pi^2}{2ma^2}n \tag{18}$$

Constants A and k are derived from the typical wave function solution, testing boundary conditions and normalizing.

ψ_n and $\Psi(x,0)$ can be used to find any c_n and then incorporated into the full sum for the total solution.

3.2 HARMONIC OSCILLATOR

In this the discussion of the harmonic oscillator will correspond to a system with $V(x) = \frac{1}{2}m\omega^2 x^2$.

This can be solved using power series, a typical, general method for solving differential equations, or using the raising and lowering operators.

Based on the physical meaninglessness of states with $E < 0$ the following statement can be made and solved (single order differential yields exponential function) for a **ground state**.

$$\hat{a}_-\psi_0 = 0 \tag{19}$$

A general form for ψ_0 in the harmonic oscillator:

$$\psi_0 = (\frac{m\omega}{\pi\hbar})^{\frac{1}{4}}e^{-\frac{m\omega}{2\hbar}x^2}, \quad E_n = (n + \frac{1}{2})\hbar\omega \tag{20}$$

From this ground state the raising operators can determine any other component. The n coefficient ensures normality.

$$\psi_n = \frac{1}{\sqrt{n!}}(\hat{a_+})^n \psi_0 \tag{21}$$

Like in the infinite square well, the components of the total function are **orthonormal.**

The raising and lowering operators are given:

$$\hat{a}_{\pm} \equiv \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega x) \tag{22}$$

3.3 THE FREE PARTICLE

$$V(x) = 0.$$

This leads to solutions that strongly resemble the infinite square well scenario, but in the case of the free particle there are no boundary conditions to be evaluated. This results in a wave function that is non-normalizable with our previous methods.

Instead working with the free particle is dependent on the relation of momentum and position, and the question is how to determine a $\phi(k)$ that matches the initial $\Psi(x)$:

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k)e^{ikx}dk \tag{23}$$

The study of Fourier analysis has given us Plancherel's theorem which give us our ϕ

$$phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{-\infty} {}^{\infty}\Psi(x,0)dx \tag{24}$$

Formalism

Quantum theory is based on wave functions and operators. The state of a function is represented as its wave function, while the observable are represented as operators.

In quantum mechanics our vector spaces are the infinity of wave functions. The meaningful space is those that are normalizable, in this case equivalent to the set of **square integrable functions** whose integral converges. This vector space is **Hilbert Space**

Inner products are represented

$$\langle f(x)^*|g(x)\rangle = \int_a^b f(x)^* g(x)dx \tag{25}$$

If f and g exist then their product exists.

Orthogonality describes two functions whose inner product is zero, and a **normalized** function describes two functions whose inner product is 1. **Orthonormality** describes a set of functions that are normalized and mutually orthogonal.

Orthogonal:
$$\langle f|g\rangle = 0.$$

Normal:
$$\langle f|g\rangle = 1.$$

Orthonormal:
$$\langle f_n|f_m\rangle = \delta_{mn}.$$

If a set of function is **complete** if any *other* function in Hilbert space can be described as a linear combination of them.

$$\sum_{n=1}^{\infty} c_n f_n(x).$$

And if this set of functions is normal, Fourier's trick applies

$$c_{n=\langle f_n|f\rangle} \tag{26}$$

4.1 OBSERVABLES AND HERMETIAN OPERATORS

Expectation values of observables are expressed neatly in this notation

$$\langle Q\rangle = \int \Psi^* \hat{Q}\Psi dx = \langle \Psi|\hat{Q}\Psi\rangle \tag{27}$$

To actually get something observable, the result must be real. And thus the operator must be Hermitian,

$$\langle f|\hat{Q}f\rangle = \langle \hat{Q}f|f\rangle, \quad \hat{Q}^\dagger = \hat{Q} \tag{28}$$

Ultimately $\hat{Q}^\dagger$ is $\hat{Q}^{*T}$, but this is a little confusing for operators like the derivative. Mostly useful for generalized proofs I think.

4.2 DETERMINATE STATES, EIGENFUNCTIONS AND DE-GENERACY

Any **determinate state**, such as the energy level of the harmonic operator, in which only certain discrete values are allowed, is an eigenfunction of its operator. For instance, $\hat{H}\Psi = E\Psi$.

Degeneracy is the phenomenon in which different eigenfunctions share the same eigenvalue. For instance in three dimensions many different wavefunction conditions can result in the same energy level, meaning that energy level is degenerate. Degeneracy is also an integer value defined by the number of eigenfunctions that share the same eigenvector.

Other wonderful properties of this are that all linear combinations of degenerate eigenfunctions are also eigenfunctions. We can also assume orthonormality between these functions.

Axiom: the eigenfunction of an observable operator are complete, any function in Hilbert space can be expressed as a linear combination of them.

4.3 GENERALIZED STATISTICAL INTERPRETATION

This, alongside the Schrodinger Equation, is the foundation of quantum mechanics.

If you measure an observable you will get an eigenvalue of the observable's associated (hermitian) operator.

The probability of getting a specific observable is

discrete:
$$|c_n|^2, \quad c_n = \langle f_n|\Psi\rangle \tag{29}$$

Continuous:
$$|c(z)|^2 dz, \quad c(z) = \langle f_z|\Psi\rangle \tag{30}$$

Thus expected values are given

$$\langle Q\rangle = \sum_n q_n |c_n|^2 \tag{31}$$

4.4 UNCERTAINTY PRINCIPLE

$$\sigma_A^2 \sigma_B^2 \geq (\frac{1}{2i}\langle[\hat{A},\hat{B}]\rangle)^2 \qquad (32)$$

4.5 THE STATE FUNCTION AND BASES

Ultimately we are dealing with one vector, the state function, in Hilbert space:

$$|S(t)\rangle$$

We operate on this function to form more familiar functions we work with. The state function in position space, formed from the position basis, is

$$\langle x|S(t)\rangle = \Psi(x,t).$$

Which shows the $\hat{x}$ operating on the state function, thus producing **an observable.**

This is all in **braket notation**

Operators

Operators are denoted with hats. Operators can be just about anything but here we use the position operator, momentum operator, Hamiltonian, raising and lowering, time evolution operator and others probably.

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \tag{33}$$

canonical commutation relation

$$[x, \hat{p}]i\hbar \tag{34}$$

$$\hat{x}\,\Psi = x\,\Psi \tag{35}$$

Momentum operator

$$\hat{p}\Psi = -i\hbar\frac{d\Psi}{dx} \tag{36}$$

A nice trick for momentum is that

$$\langle p \rangle = \frac{d\langle x \rangle}{dt} \tag{37}$$

In practice they look as follows:

$$\langle \text{KE} \rangle = \int \Psi^* \frac{\hat{p}^2}{2m}\Psi\,dx \tag{38}$$

6
Three Dimensions

7
class

1. J : total angular momentum (orbital + spin)
2. m_j the z-component of the total angular momentum
3. l orbital angular momentum
4. m_l z-component of the orbital angular momentum
5. s spin angular momentum
6. m_s z-component of spin angular momentum

Angular Momentum and Spin

8.1 OVERVIEW, COMMONALITY

$\hat{L}$ and $\hat{S}$ must satisfy

$$\hat{Q}^2 \left| sm \right\rangle = \hbar^2 q(q+1) \left| sm \right\rangle, \quad \hat{Q}_z \left| sm \right\rangle = \hbar m \left| sm \right\rangle \qquad (39)$$

$$\hat{Q}_\pm \left| sm \right\rangle = \hbar \sqrt{q(q+1) - m(m \pm 1)} \left| s(m \pm 1) \right\rangle \qquad (40)$$

Where $\hat{Q}$ is $\hat{L}$ or $\hat{S}$ and q is the total angular momentum or the inherent spin of the particle.

Raising operators are defined

$$Q_\pm \equiv Q_x \pm i Q_y \qquad (41)$$

8.2 ANGULAR MOMENTUM

owen note: can probably incorporate the spherical haronic revelation earlier for compactness

Angular momentum is defined by

$$L = r \times p \qquad (42)$$

which expands to (cartiesian)

$$L_x = y p_z - z p_y, \quad L_y = z p_x - x p_z, \quad L_z = x p_y - y p_x \qquad (43)$$

These do not commute,

$$[L_x, L_y] = i\hbar L_z; \quad [L_y, L_z] = i\hbar L_x; \quad [L_z, L_x] = i\hbar L_y \qquad (44)$$

Thus the components of angular momentum are incompatible observables and follow the uncertainty principle.

The square of the total angular momentum does commute with each component and

$$L^2 = L_x^2 + L_y^2 + L_z^2 \qquad (45)$$

Luckily L^2 commutes with any component of L, meaning simultaneous eigenstates can be found between L^2 and L_z.

We use a similar technique to the raising and lowering operators as we did for the one dimensional harmonic oscillator. Here the raising and lowering operators change m, the level of angular momentum.

$$L_\pm \equiv L_x \pm iL_y \tag{46}$$

Squaring this definition gives a new expression for L^2. We can use this with the face that L_z, L^2, and $L \pm f$ all may share an eigenfunction (here f), along with the condition that there must be some maximum angular momentum so that $L_+ f = 0$, to find

$$L^2 f = \hbar^2 \ell(\ell+1)f \tag{47}$$

Where ℓ represents the highest angular momentum state possible in L_z, and m represents the angular momentum in the z component.

The same can be said with the lowering operator to show that the **lowest allowed state is** $-\ell$.

The two essential eigenstates of angular momentum are

$$L^2 f_\ell^m = \hbar^2 \ell(\ell+1)f_\ell^m, \quad L_z f_\ell^m = \hbar m_\ell^m \tag{48}$$

8.2.1 Spherical Angular Momentum

The components of angular momentum can easily be found first by using the spherical Laplacian and then decomposing unit spherical vectors into cartesian functions and ϕ, θ functions:

$$L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cos\phi \cot\theta \frac{\partial}{\partial\phi} \right) \tag{49}$$

$$L_y = -i\hbar \left(\sin\phi \frac{\partial}{\partial\theta} - \sin\phi \cot\theta \frac{\partial}{\partial\phi} \right) \tag{50}$$

$$L_z = -i\hbar \frac{\partial}{\partial\phi} \tag{51}$$

$$L_\pm = \pm^{\pm i\phi} \left(\frac{\partial}{\partial\theta} \pm i \cot\theta \frac{\partial}{\partial\phi} \right) \tag{52}$$

The similar method of constructing L^2 and finding the eigenfunctions ultimately leads to finding the eigenfunctions to be the **spherical harmonics**, Y_m^ℓ, so that

$$H\psi = E\psi, \quad L^2\psi = \hbar^2 \ell(\ell+1)\psi, \quad L_z\psi = \hbar m\psi \tag{53}$$

8.3 SPIN

Spin corresponds to a magnetic property of a particle. Spin is an inherent property of particles.

The spin of a particle represents the number of spin states it could be in, i.e. a spin $\frac{3}{2}$ particle could be in any state from $-\frac{3}{2}\hbar$ to $\frac{3}{2}\hbar$.

Spin is mathematically analogous to angular momentum, but ultimately we do not know what spin is.

Each dimension has its own, independent spin. When put through a magnetic field, spin up electrons deflect in the direction of the magnetic field and vice versa. These selected spin up and spin down electrons are only in one direction. The others are unceratain (as in angular momentum case)

Rather than being derivative operators the spin operators are conveniently represented as matrix operators. We use z as the default spin direction

The spin states of a particle (in the z component) ranges in integer steps from $m = -s$ to $m = s$ either as multiples of $\frac{1}{2}\hbar$ or $\hbar$.

8.3.1 Spin one-half

For a spin $\frac{1}{2}$ particle there are only two states, up and down. Represented $|\frac{1}{2}\frac{1}{2}\rangle$ and $|\frac{1}{2}(-\frac{1}{2})\rangle$ The first number in the ket represents the intrinsic spin, s, and the second represents the spin state, m. This can be represented conveniently with basis vectors

$$\chi = \begin{bmatrix} 1 \\ 0 \end{bmatrix} = a\chi_+ + b\chi_-, \quad \chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad \chi_- \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{54}$$

9

cleanup below

sectionSolution for Hydrogen atom

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\frac{r}{na}} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)\right] Y_l^m \quad (55)$$

9.0.1 Dirac Delta

$$\int f(x)\delta(x-a)dx = f(a) \int \delta(x-a)dx = f(a) \quad (56)$$