2.5. Expectation values and operators

For a review on probabilities (discrete/continuous variables) see Griffiths, Chapter 1.3, and/or Appendix C.

Besides the (total) probability to find the particle in a certain range of \( x \) (or volume in \( \mathbb{R}^3 \)) are there any other measurable quantities resulting from the wave function.

Yes! An important one is the expectation value

\[
\langle \hat{\tau} \rangle_t = \int_{\mathbb{R}^3} \hat{\tau} \, |\psi(\vec{r}, t)|^2 \, d\vec{r}
\]

\[
= \int_{\mathbb{R}^3} \, \tau(\vec{r}, t) \, \hat{\tau}(\vec{r}, t) \, d\vec{r}
\]

It is the average value over the results of many measurements of identically prepared systems (ensemble of particles).

Important: This not measurement of the system over and over again.

Compare: For a discrete variable, the average value \( \langle \tau \rangle \) is given by

\[
\langle \tau \rangle = \sum_j \tau_j \, P_j
\]

where \( P_j \) is the probability for a certain value \( j \). Do you see the analogy to the above definition for a continuous variable \( \hat{\tau} \) where \( |\psi(\vec{r}, t)|^2 \) is the probability density.
We now define the expectation value of the momentum of a particle (in analogy to classical mechanics) as:

\[ \langle \vec{p} \rangle_t = m \frac{d}{dt} \langle \vec{r} \rangle_t = m \frac{d}{dt} \int \tau^*(\vec{r}, t) \tau(\vec{r}, t) \, d\vec{r} \]

\[ = m \int \left( \frac{d \tau^*(\vec{r}, t)}{dt} \right) \tau(\vec{r}, t) \, d\vec{r} + \int \tau^*(\vec{r}, t) \tau \left( \frac{d \tau(\vec{r}, t)}{dt} \right) \, d\vec{r} \]

\[ = \frac{m}{i\hbar} \int \left( -\frac{\hbar^2}{2m} \Delta \tau^* + V \tau^* \right) \tau \, d\vec{r} \]

Use Schrödinger equation

\[ + \frac{m}{i\hbar} \int \tau^* \nabla \left( -\frac{\hbar^2}{2m} \Delta \tau + V \tau \right) \, d\vec{r} \]

\[ = \frac{\hbar}{2i} \int \left( \Delta \tau^* \right) \tau \tau - \tau^* \tau \left( \Delta \tau \right) \, d\vec{r} \]

Potential terms cancel.

Look at x-component (other components analogous)

\[ \langle p_x \rangle_t = \frac{\hbar}{2i} \int \left( \Delta \tau^* \right) \tau \tau - \tau \tau \left( \Delta \tau \right) \, dx \, dy \, dz \]

\[ = \frac{\hbar}{2i} \int \left( \frac{\partial^2}{\partial x^2} \tau^* \right) \tau - \tau \tau \left( \frac{\partial^2}{\partial x^2} \tau \right) \, d\vec{r} \]

\[ \frac{\partial^2}{\partial y^2}, \frac{\partial^2}{\partial z^2} \] are zero (summands cancel).

Use:

\[ \left( \frac{\partial^2}{\partial x^2} \tau^* \right) \tau = \frac{\partial}{\partial x} \left[ \left( \frac{\partial}{\partial x} \tau^* \right) \tau \right] \]

\[ = \left( \frac{\partial}{\partial x} \tau^* \right) \tau - \left( \frac{\partial}{\partial x} \tau \right) \left( \frac{\partial}{\partial x} \tau^* \right) \]

Same for second term.
\[ <p_x> = \frac{\hbar}{2i} \int \frac{2}{\partial x} \left[ \left( \frac{\partial}{\partial x} t^* \right) x t - \left( \frac{\partial}{\partial x} t^* \right) t - \left( \frac{\partial}{\partial x} t \right) \left( \frac{\partial}{\partial x} t^* \right) \right] \, dx \]

\[ = \frac{\hbar}{2i} \int \left( \frac{\partial t^*}{\partial x} \right) x t - \frac{\partial t^*}{\partial x} \left( \frac{\partial t}{\partial x} \right) \, |^{x=\infty}_{x=-\infty} \, dy \, dz \]

\[ = 0 \quad \text{(since } t \to 0 \text{ for } x \to \pm \infty) \]

\[ + \frac{\hbar}{2i} \int t^* \frac{\partial t^*}{\partial x} - t \frac{\partial}{\partial x} t \, d\tau \]

\[ = \int t^* t \, |^{x=\infty}_{x=-\infty} \, dy \, dz - \int t^* \frac{\partial t}{\partial x} \, d\tau \]

\[ = 0 \quad \text{(see above)} \]

\[ = \frac{2\hbar}{2i} \int t^* \frac{\partial t}{\partial x} \, d\tau = \int t^* \left( -i\hbar \frac{\partial}{\partial x} \right) t \, d\tau \]

In all dimensions: \[ <\hat{p}> = \int t^* \left( -i\hbar \hat{\nabla} \right) t \, d\tau \]

Expectation values of a physical variable can therefore be given with the help of the wavefunction as:

\[ <x> = \int t^* (x) t \, d\tau \]

\[ <y> = \int t^* (y) t \, d\tau \]

\[ <p_x> = \int t^* \left( -i\hbar \frac{\partial}{\partial x} \right) t \, d\tau \]

\[ <\hat{p}> = \int t^* \left( -i\hbar \hat{\nabla} \right) t \, d\tau \]
The expression in brackets \((\quad)\) are operators (here: multiplication and differential operators). Formally: An operator is an instruction which assigns a (wave-) function \(f(x)\) a new (wave-) function \(g(x)\)
\[
\hat{O} : f(x) \rightarrow \hat{O} f(x) = g(x)
\]
\[
- \frac{i\hbar}{\partial x} : f(x) \rightarrow - i\hbar \frac{\partial}{\partial x} f(x) = g(x)
\]

We call:
\((\mathbf{x,} \mathbf{)}\) the \(x\)-operator
\((-i\hbar \frac{\partial}{\partial x})\) the \(\hat{P}_x\)-operator
\((-i\hbar \hat{\mathbf{V}})\) the momentum operator
\((\hat{\mathbf{P}})\) the position operator

We assign every observable \(A\) an operator \(\hat{A}\) such that the expectation value of \(A\) in state \(\hat{\psi}\) is given by
\[
\langle A \rangle_t = \int \hat{\psi}^*(\mathbf{\hat{P}}, \mathbf{\hat{x}}, t) \hat{A} \hat{\psi}(\mathbf{\hat{P}}, \mathbf{\hat{x}}, t) \, d\mathbf{\hat{x}}
\]

Every observable \(A\), which is given in classical mechanics by \(F(x_i, p_j)\), we assign an operator
\[
\hat{A} = F(\hat{\mathbf{x}}, \hat{\mathbf{p}}) = F(x_i, -i\hbar \frac{\partial}{\partial x_i})
\]

This is called the correspondence principle.
Notes about observables and operators:

- The complex conjugate $\bar{z}$ of a complex number $z$ is also called Hermitian adjoint $z^\dagger$. Analogously, the Hermitian adjoint $\hat{A}^\dagger$ of an operator $\hat{A}$ is defined by

$$\int \chi^\dagger(\mathbf{r},t) \hat{A}^\dagger \chi(\mathbf{r},t) = \left[ \int \chi^\dagger(\mathbf{r},t) \hat{A} \chi(\mathbf{r},t) \right]^*$$

expectation values are observables

$$\Rightarrow \text{real number}$$

$$\Rightarrow \hat{A} = \hat{A}^\dagger \Rightarrow \text{the operator is Hermitian}$$

- To represent an observable the operator $\hat{A}$ has to be linear (superposition principle)

$$\hat{A} (\alpha_1 \chi_1 + \alpha_2 \chi_2) = \alpha_1 \left( \hat{A} \chi_1 \right) + \alpha_2 \left( \hat{A} \chi_2 \right)$$

$$\Rightarrow \text{An observable has to be represented by a linear Hermitian operator.}$$

- Important observables:

**Kinetic energy:** $E_{\text{kin}} = T = \frac{1}{2m} \left( p_x^2 + p_y^2 + p_z^2 \right)$

$$\Rightarrow \hat{T} = \frac{1}{2m} \left[ (-i\hbar \frac{\partial}{\partial x})^2 + (-i\hbar \frac{\partial}{\partial y})^2 + (-i\hbar \frac{\partial}{\partial z})^2 \right] = \frac{\hbar^2}{2m} \Delta$$

**Potential energy:** $V(\mathbf{r}) \Rightarrow \hat{V}(x, y, z)$

$$\Rightarrow T + V \equiv \hat{H}(\mathbf{r}, \mathbf{p}) \Rightarrow \hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \Delta + V(\mathbf{r})$$

Hamilton-Operator

Reminder: $i\hbar \frac{\partial}{\partial t} \chi(\mathbf{r},t) = \left( -\frac{\hbar^2}{2m} + V(\mathbf{r}) \right) \chi(\mathbf{r},t) = \hat{H} \chi(\mathbf{r},t)$
Thus, we postulate (Careful! We did not derive it!!)

The Schrödinger equation for any \( N \)-particle system, which is described by the wave function \( \psi(\vec{r}_1, ..., \vec{r}_n; t) \)

is given by

\[
\frac{i\hbar}{\partial t} \psi(\vec{r}_1, ..., \vec{r}_n; t) = \hat{H} \psi(\vec{r}_1, ..., \vec{r}_n; t)
\]

where \( \hat{H} \) is the operator assigned to the Hamilton function \( H(\vec{r}_1, ..., \vec{r}_n; t) \) in classical mechanics.

- Ehrenfest theorem

\[
\frac{d}{dt} \langle \hat{P} \rangle = \langle -\nabla V(\vec{r}) \rangle
\]

The expectation value in quantum mechanics obey the same equation of motion as the corresponding variables in classical mechanics.

- Temporal dynamics of expectation values

\[
-i\hbar \frac{\partial}{\partial t} \langle \hat{A} \rangle = \int \left( i\hbar \frac{\partial}{\partial t} \right) \hat{A} \psi^* \, d\vec{r} + \int \psi^* \left( \frac{i\hbar}{\partial t} \hat{A} \right) \psi \, d\vec{r} \\
+ \int \psi^* \hat{A} \left( \frac{i\hbar}{\partial t} \psi \right) \, d\vec{r}
\]

Use Schrödinger equation: \( i\hbar \frac{\partial}{\partial t} \psi = \hat{H} \psi \)

\[
- i\hbar \frac{\partial}{\partial t} \psi^* = (\hat{H} \psi)^*
\]
\[
\frac{i\hbar}{2} < \dot{A} > = - \int (\hat{H} +)^* \dot{A} + d\varphi + i\hbar \int [\hat{A} (\hat{H} +) + d\varphi + \int [\hat{A} (\hat{H} +) d\varphi
\]

In order to combine the first and the third summand we show \((\hat{H} +)^* = \hat{T}^* \hat{H}\).

We know: \(< \hat{A} > = < \hat{A} >^* \): Energy operator, expectation value has to be real.

\[
\Rightarrow \int \hat{T}^* \hat{H} + d\varphi = \int \hat{H}^* \hat{T}^* d\varphi
\]

\[
\Rightarrow \int \hat{T}^* \hat{H} + - (\hat{H} +)^* \hat{T}^* d\varphi = 0
\]

\[
\Rightarrow \int [\hat{T}^* \hat{H} - (\hat{H} +)^* \hat{T}^*] d\varphi = 0
\]

Actually, we have just shown (again) that \(\hat{H}\) is a Hamiltonian operator.

\((\text{Do you see it?})\)

\[
\Rightarrow \frac{i\hbar}{2} < \dot{A} > = \int [\hat{A} \hat{H} - \hat{H} \hat{A}] + d\varphi + i\hbar < \frac{\partial \hat{A}}{\partial t}
\]

\[
= < [\hat{A}, \hat{H}] > + i\hbar < \frac{\partial \hat{A}}{\partial t}
\]

if \(\hat{A}\) depends on time

The expectation value of a variable in state \(\hat{T}\) is time independent if and only if \(\hat{A}\) commutes with the Hamiltonian operator \(\hat{H}\).