Review of Quantum Mechanics I

- <u>Operators in Quantum Mechanics</u>
  - The energy-momentum relation is given by

$$E = \frac{p^2}{2m} + V\left(\vec{r}, t\right).$$

  - Multiply this by the wave function to obtain

$$E\Psi = \frac{p^2}{2m}\Psi + V\Psi.$$

  - Replace the quantities *E* and *p* by the following operators

$$E \to \hat{E} = i\hbar\frac{\partial}{\partial t} \qquad \text{and} \qquad p_n \to \hat{p}_n = -i\hbar\frac{\partial}{\partial x_n}.$$

  - Using this formal replacement of classical quantities by the corresponding operators gives us

$$\hat{E}\Psi = \frac{\hat{p}^2}{2m}\Psi + V\Psi \quad \to \quad i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi + V\left(\vec{r}, t\right)\Psi.$$

Review of Quantum Mechanics I

- Normalization and Moments
  - Assume that we describe the bound state of a single particle. Then we require that the following normalization condition is satisfied

$$\int d^3r \ \Psi(\vec{r},t)\Psi^*(\vec{r},t) = 1.$$

  - Consider the time-independent one-dimensional case. Then we have

$$\Psi(\vec{r},t) = \Psi(x).$$

  - In this case the normalization condition becomes simply

$$\int_{-\infty}^{+\infty} dx \ \Psi(x)\Psi^*(x) = 1.$$

  - We define the *n*th moment via

$$\langle x^n \rangle = \int_{-\infty}^{+\infty} dx \ \Psi(x) x^n \Psi^*(x).$$

Review of Quantum Mechanics I

- <u>The Heisenberg Uncertainty Relation</u>
  - Consider a simple 1D Gaussian wave of the form

    $$\Psi(x) = \Psi_0 e^{-ax^2}.$$

  - Determine the constant Ψ_0 via the normalization condition

    $$\int_{-\infty}^{+\infty} dx\ \Psi(x)\Psi^*(x) = \Psi_0\Psi_0^* \int_{-\infty}^{+\infty} dx\ e^{-2ax^2} \overset{!}{=} 1.$$

  - By using the Gaussian integral

    $$\int_0^{\infty} dx\ e^{-bx^2} = \frac{\sqrt{\pi}}{2\sqrt{b}}$$

    we find

    $$\Psi_0\Psi_0^* \int_{-\infty}^{+\infty} dx\ e^{-2ax^2} = \Psi_0\Psi_0^* \sqrt{\frac{\pi}{2a}} = 1.$$

Review of Quantum Mechanics I

- <u>The Heisenberg Uncertainty Relation</u>
  - Therefore, we find

$$\Psi_0 \Psi_0^* = \sqrt{\frac{2a}{\pi}}.$$

  - The second moment is given by

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} dx\ \Psi(x) x^2 \Psi^*(x) = \Psi_0 \Psi_0^* \int_{-\infty}^{+\infty} dx\ x^2 e^{-2ax^2} = \frac{1}{4a}.$$

  - We use the <u>Fourier transforms</u>

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk\ \Phi(k) e^{ikx}$$

$$\Phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx\ \Psi(x) e^{-ikx}.$$

Review of Quantum Mechanics I

- <u>The Heisenberg Uncertainty Relation</u>
  - Compute the Fourier transform of the Gaussian

$$\begin{aligned}\Phi(k) &= \frac{\Psi_0}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} dx\; e^{-ax^2}e^{-ikx} \\ &= \frac{\Psi_0}{\sqrt{2a}}e^{-k^2/(4a)}.\end{aligned}$$

Is also a Gaussian!!!

  - Calculate the second moment in Fourier space

$$\begin{aligned}\langle k^2\rangle &= \int_{-\infty}^{+\infty} dk\; \Phi(k)k^2\Phi^*(k) \\ &= \frac{\Psi_0\Psi_0^*}{2a}\int_{-\infty}^{+\infty} dk\; k^2 e^{-k^2/(2a)} \\ &= a.\end{aligned}$$

Review of Quantum Mechanics I

- <u>The Heisenberg Uncertainty Relation</u>
  - We derived for the two moments

$$\langle x^2 \rangle = \frac{1}{4a}$$
$$\langle k^2 \rangle = a.$$

  - Therefore, we find for the product of the two second moments

$$\langle x^2 \rangle \langle k^2 \rangle = \frac{1}{4}.$$

This is a property of the Fourier transform!

  - Note that the widths of the two Gaussians are

$$\Delta x = \sqrt{\langle x^2 \rangle} = \frac{1}{2\sqrt{a}}$$
$$\Delta k = \sqrt{\langle k^2 \rangle} = \sqrt{a}.$$

Review of Quantum Mechanics I

- <u>The Heisenberg Uncertainty Relation</u>
  - For the product of the two widths we, therefore, obtain

$$\Delta x \Delta k = \frac{1}{2}.$$

  - Using the de Broglie relation $p = \hbar k$, this becomes

$$\Delta x \Delta p = \frac{\hbar}{2}.$$

  - Note that this was derived for a Gaussian wave. In general we have

$$\Delta x \Delta p \geq \frac{\hbar}{2}.$$

  - This is the famous uncertainty relation!
  - The proof will be discussed later.

Review of Quantum Mechanics I

- <u>The Continuity Equation</u>
  - Schrödinger's equation is given by

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi + V\left(\vec{r},t\right)\Psi.$$

  - Its complex conjugate is

Assume a real potential

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\Delta\Psi^* + V\left(\vec{r},t\right)\Psi^*.$$

  - Remember that the probability density is $\Psi\Psi^*$.
  - The time-derivative of the probability density is

$$\frac{\partial}{\partial t}\Psi\Psi^* = \Psi\frac{\partial\Psi^*}{\partial t} + \Psi^*\frac{\partial\Psi}{\partial t}.$$

Use Schrödinger's equation

Review of Quantum Mechanics I

- <u>The Continuity Equation</u>
  - With the help of the Schrödinger equation we derive

$$\begin{aligned}
\frac{\partial}{\partial t}\Psi\Psi^* &= \Psi\frac{\partial\Psi^*}{\partial t} + \Psi^*\frac{\partial\Psi}{\partial t} \\
&= \frac{\Psi}{-i\hbar}\left[-\frac{\hbar^2}{2m}\Delta\Psi^* + V\Psi^*\right] + \frac{\Psi^*}{i\hbar}\left[-\frac{\hbar^2}{2m}\Delta\Psi + V\Psi\right] \\
&= \frac{\hbar}{2im}\Psi\Delta\Psi^* - \frac{1}{i\hbar}V\Psi^*\Psi - \frac{\hbar}{2im}\Psi^*\Delta\Psi + \frac{1}{i\hbar}V\Psi\Psi^* \\
&= \frac{\hbar}{2im}\Big(\Psi\Delta\Psi^* - \Psi^*\Delta\Psi\Big).
\end{aligned}$$

  - To rewrite this we consider the following (just product rule)

$$\begin{aligned}
\vec{\nabla}\cdot\Big(\Psi\vec{\nabla}\Psi^*\Big) &= \vec{\nabla}\Psi\cdot\vec{\nabla}\Psi^* + \Psi\Delta\Psi^* \\
\vec{\nabla}\cdot\Big(\Psi^*\vec{\nabla}\Psi\Big) &= \vec{\nabla}\Psi^*\cdot\vec{\nabla}\Psi + \Psi^*\Delta\Psi.
\end{aligned}$$

Subtract these two equations

Review of Quantum Mechanics I

- The Continuity Equation
  - By combining all this, we derive

$$\frac{\partial}{\partial t}\Psi\Psi^* = \frac{\hbar}{2im}\Big(\Psi\Delta\Psi^* - \Psi^*\Delta\Psi\Big) = -\vec{\nabla}\cdot\left[\frac{\hbar}{2im}\Big(\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*\Big)\right].$$

  - For the probability density we can use $\rho=\Psi\Psi^*$.
  - Furthermore, we define the particle current density via

$$\vec{j} := \frac{\hbar}{2im}\Big(\Psi^*\vec{\nabla}\Psi - \Psi\vec{\nabla}\Psi^*\Big).$$

  - Using this above yields

$$\frac{\partial}{\partial t}\rho + \vec{\nabla}\cdot\vec{j} = 0.$$

This is a typical continuity equation.

Review of Quantum Mechanics I

➢ <u>The Continuity Equation</u>

- We found the continuity equation

$$\frac{\partial}{\partial t}\rho + \vec{\nabla}\cdot\vec{j} = 0.$$

- Integrating this over the volume V yields

$$\int_V d^3r \, \frac{\partial \rho}{\partial t} = -\int_V d^3r \, \vec{\nabla}\cdot\vec{j}.$$

- We rewrite the left-hand-side and for the right-hand-side we use the <u>divergence theorem</u> to derive

$$\frac{d}{dt}\int_V d^3r \, \rho = -\int_{\partial V} d\vec{S}\cdot\vec{j}.$$

Describes conservation of particles!

Number of particles in V

Particle flux through surface of the volume V

Review of Quantum Mechanics I

- Momentum in Wave Mechanics
  - In classical mechanics momentum is given by

$$\vec{p} = m\vec{v} = m\frac{d}{dt}\vec{r}.$$

  - We now consider the following

$$\langle \vec{p}\, \rangle = m\frac{d}{dt}\langle \vec{r}\, \rangle.$$

  - To make this easier we consider the 1D case (*x*-direction).
  - Using the definition of the first moment / expectation value yields

$$\begin{aligned} \langle p \rangle &= m\frac{d}{dt}\int dx\ \Psi^* x \Psi \\ &= m\int dx\ \left(\frac{\partial \Psi^*}{\partial t} x\Psi + \Psi^* x \frac{\partial \Psi}{\partial t}\right). \end{aligned}$$

Use Schrödinger's eq.

Review of Quantum Mechanics I

- <u>Momentum in Wave Mechanics</u>
  - After using the Schrödinger equation in the formula for the expecation value, we obtain

$$
\begin{aligned}
\langle p \rangle &= m \int dx \left(\frac{\partial \Psi^*}{\partial t} x \Psi + \Psi^* x \frac{\partial \Psi}{\partial t} \right) \\
&= \frac{m}{i\hbar} \int dx \left(\frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2} x \Psi - V \Psi^* x \Psi \right) \\
&- \frac{m}{i\hbar} \int dx \left(\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} x \Psi^* - V \Psi x \Psi^* \right) \\
&= \frac{\hbar}{2i} \int dx \left(\frac{\partial^2 \Psi^*}{\partial x^2} x \Psi - \frac{\partial^2 \Psi}{\partial x^2} x \Psi^* \right).
\end{aligned}
$$

  - To rewrite this we use integration by parts.

Review of Quantum Mechanics I

➢ <u>Momentum in Wave Mechanics</u>

- After integration by parts we find

$$
\begin{aligned}
\langle p \rangle &= \frac{\hbar}{2i}\int dx\,\Big(\frac{\partial^2\Psi^*}{\partial x^2}x\Psi - \frac{\partial^2\Psi}{\partial x^2}x\Psi^*\Big) \\
&= -\frac{\hbar}{2i}\int dx\,\Big[\frac{\partial\Psi^*}{\partial x}\Big(\Psi + \cancel{x\frac{\partial\Psi}{\partial x}}\Big) - \frac{\partial\Psi}{\partial x}\Big(\Psi^* + \cancel{x\frac{\partial\Psi^*}{\partial x}}\Big)\Big] \\
&= -\frac{\hbar}{2i}\int dx\,\Big(\frac{\partial\Psi^*}{\partial x}\Psi - \frac{\partial\Psi}{\partial x}\Psi^*\Big).
\end{aligned}
$$

- To continue we use integration by parts for the first term to obtain

$$
\begin{aligned}
\langle p \rangle &= -\frac{\hbar}{2i}\int dx\,\Big(-2\Psi^*\frac{\partial\Psi}{\partial x}\Big) \\
&= \int dx\,\Psi^*\Big(-i\hbar\frac{\partial}{\partial x}\Big)\Psi.
\end{aligned}
$$

Momentum operator!

Review of Quantum Mechanics I

- Momentum in Wave Mechanics
  - We conclude that momentum is represented by the operator

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}.$$

  - In 3D this becomes

$$\hat{\vec{p}} = -i\hbar\vec{\nabla}.$$

  - Note, we derived

$$\langle p\rangle = \int dx\ \Psi^*\Big(-i\hbar\frac{\partial}{\partial x}\Big)\Psi = \int dx\ \Psi^*\Big(\hat{p}\Psi\Big).$$

  - We can use again integration by parts to write

$$\langle p\rangle = \int dx\ \Psi\Big(i\hbar\frac{\partial}{\partial x}\Big)\Psi^* = \int dx\ \Psi\Big(\hat{p}\Psi\Big)^*.$$

Review of Quantum Mechanics I

➢ <u>Hermitian Operators</u>

- We found for the momentum operator the following relation

$$\langle p \rangle = \int dx\ \Psi^* \Big(\hat{p}\Psi \Big) = \int dx\ \Psi \Big(\hat{p}\Psi \Big)^*.$$

- In general we call an operator $\hat{A}$ an <u>Hermitian operator</u> if it satisfies

$$\int dx\ \Phi^* \Big(\hat{A}\Psi \Big) = \int dx\ \Psi \Big(\hat{A}\Phi \Big)^*.$$

- We defined the expectation value of an operator $\hat{A}$ via

$$\langle \hat{A} \rangle := \int dx\ \Psi^* \Big(\hat{A}\Psi \Big).$$

- The complex conjugate is then

$$\langle \hat{A} \rangle^* = \int dx\ \Psi \Big(\hat{A}\Psi \Big)^*.$$

Charles Hermite

- We conclude: <u>if an operator is Hermitian, its expectation value is real!</u>

Review of Quantum Mechanics I

- <u>The Hamiltonian Operator</u>
  - We now go back to Schrödinger's equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \Delta \Psi + V \Psi.$$

  - We can write the right-hand side via

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= \frac{1}{2m} \left(-i\hbar \vec{\nabla} \right)^2 \Psi + V \Psi \\ &= \frac{1}{2m} \left(\hat{\vec{p}} \right)^2 \Psi + V \Psi \\ &= \left(\frac{1}{2m} \hat{\vec{p}}^{\,2} + V \right) \Psi. \end{aligned}$$

  - The following operator is called the <u>Hamiltonian operator</u>

$$\hat{H} := \frac{1}{2m} \hat{\vec{p}}^{\,2} + V.$$

See Classical Mechanics II for more about the Hamiltonian!

Sir William R. Hamilton

Review of Quantum Mechanics I

- <u>Wave Functions in Momentum Space</u>
  - In 1D the Fourier transform is given by

$$\Psi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dk \; \Phi(k) e^{ikx}$$

$$\Phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dx \; \Psi(x) e^{-ikx}.$$

  - However, in quantum mechanics we prefer to use momentum $p = \hbar k$ instead of wave number k. Therefore, we use

$$\Psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dp \; \Phi(p) e^{ipx/\hbar}$$

$$\Phi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx \; \Psi(x) e^{-ipx/\hbar}.$$

Review of Quantum Mechanics I

- Wave Functions in Momentum Space
  - Check whether *Φ(p)* is normalized by performing the following calculations

$$\int dp\, \Phi^*(p)\Phi(p) = \frac{1}{2\pi\hbar}\int dp \int dx\, \Psi^*(x)e^{ipx/\hbar}\int dx'\, \Psi(x')e^{-ipx'/\hbar}$$
$$= \frac{1}{2\pi}\int dx \int dx'\, \Psi^*(x)\Psi(x')\int dk\, e^{ik(x-x')}.$$

  - To evaluate the *k*-integral we use the (very important) relation

$$\int_{-\infty}^{+\infty} dk\, e^{ik(x-x')} = 2\pi\delta\left(x - x'\right).$$

$$\int_{-\infty}^{+\infty} dx\, f(x)\,\delta(x - x_0) = f(x_0)$$

Dirac‘s delta

  - Therewith we derive

$$\int dp\, \Phi^*\Phi = \int dx \int dx'\, \Psi^*(x)\Psi(x')\delta\left(x - x'\right) = \int dx\, \Psi^*(x)\Psi(x) = 1.$$

Review of Quantum Mechanics I

- <u>Wave Functions in Momentum Space</u>
  - By performing this type of calculation one can easily show that

$$\langle p \rangle = \int_{-\infty}^{+\infty} dp \, \Phi^*(p) \, p \, \Phi(p)$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} dp \, \Phi^* \left(i\hbar \frac{\partial}{\partial p} \right) \Phi.$$

  - We conclude that in momentum space

$$\hat{x} = i\hbar \frac{\partial}{\partial p} \qquad \text{and} \qquad \hat{p} = p.$$

  - In configuration space (x-space), on the other hand, we found

$$\hat{x} = x \qquad \text{and} \qquad \hat{p} = -i\hbar \frac{\partial}{\partial x}.$$

Review of Quantum Mechanics I

- <u>The Commutation Relation</u>
  - Problem: what happens if we have products of operators?
  - In classical physics we have *xp* = *px*. What about QM?
  - Consider the following product in configuration space

$$\hat{x}\hat{p}\Psi = x\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi.$$

  - Then, on the other hand, we have

$$\hat{p}\hat{x}\Psi = \frac{\hbar}{i}\frac{\partial}{\partial x}(x\Psi) = \frac{\hbar}{i}\left(\Psi + x\frac{\partial\Psi}{\partial x}\right).$$

This is not the same!

  - Consider the following

$$(\hat{p}\hat{x} - \hat{x}\hat{p})\Psi = \frac{\hbar}{i}\left(\Psi + x\frac{\partial\Psi}{\partial x}\right) - x\frac{\hbar}{i}\frac{\partial}{\partial x}\Psi = -i\hbar\Psi.$$

Review of Quantum Mechanics I

- <u>The Commutation Relation</u>
  - We found

$$\left(\hat{p}\hat{x} - \hat{x}\hat{p}\right)\Psi = -i\hbar\Psi.$$

  - This result does not depend on the wave function Ψ!
  - We define the <u>commutation relation</u> (short: the <u>commutator</u>) via

$$\left[\hat{A}, \hat{B}\right] := \hat{A}\hat{B} - \hat{B}\hat{A}.$$

  - Therewith we can write

$$\left[\hat{p}, \hat{x}\right] = -i\hbar.$$

This is related to Heisenberg's uncertainty relation!

  - Additional rule used in QM (e.g., in the Hamiltonian operator)

$$pf(x) \quad \rightarrow \quad \frac{\hat{p}f(x) + f(x)\hat{p}}{2}.$$

Review of Quantum Mechanics I

➢ <u>The Time-Dependent Schrödinger Equation</u>

- We consider the one-dimensional but time-dependent equation

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + V(x)\Psi(x,t).$$

- Note, we consider a potential which does not depend on time!
- Partial Differential Equations (PDEs) are usually solved via the product *ansatz*

$$\Psi(x,t) = T(t)u(x).$$

- Using this in the Schrödinger equation yields

$$i\hbar u(x)\frac{\partial T(t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2} + V(x)u(x)\right]T(t).$$

Review of Quantum Mechanics I

- <u>The Time-Dependent Schrödinger Equation</u>
  - To continue we divide the equation

$$i\hbar u(x)\frac{\partial T(t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2} + V(x)u(x)\right]T(t)$$

  by *u(x)T(t)* to find

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2 u(x)}{\partial x^2} + V(x)u(x)\right]\frac{1}{u(x)}.$$

  - Both sides of this equation depend on different variables, namely t and x.
  - Since this equation must be correct for all t and x, both sides are constant.
  - We denote this constant by E since it is related to energy.

Review of Quantum Mechanics I

- <u>The Time-Dependent Schrödinger Equation</u>
  - Therefore, we find two equations.
  - The first equation is

$$i\hbar \frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = E \qquad \text{with} \qquad E = const.$$

  - This can easily be written as

$$\frac{\partial T(t)}{\partial t} = -\frac{iE}{\hbar} T(t).$$

  - This very basic Ordinary Differential Equation (ODE) has the solution

$$T(t) = Ce^{-iEt/\hbar} \qquad \text{with} \qquad C = const.$$

Review of Quantum Mechanics I

- <u>The Time-Dependent Schrödinger Equation</u>
  - The second equation is

$$-\frac{\hbar^2}{2m}\frac{d^2u(x)}{dx^2} + V(x)u(x) = Eu(x).$$

  - This equation is often called the <u>time-independent Schrödinger</u> equation.
  - Note, in 3D this equation is still a PDE with the three variables *(x,y,z)* or in spherical coordinates *(r,Θ,Φ)*.
  - This equation is a so-called <u>eigenvalue equation</u>.
  - Alternatively, we can write this equation as

$$\hat{H}u(x) = Eu(x).$$

Hamiltonian operator → $\hat{H}$

Energy eigenvalues → E

Eigenfunctions → $u(x)$

Review of Quantum Mechanics I

- The Time-Dependent Schrödinger Equation
  - The solution of

    $$\hat{H}u(x) = Eu(x)$$

    provides the eigenvalues E as well as the eigenfunctions $u(x)$.
  - The eigenfunctions depend on E as well. Therefore, we often write

    $$\hat{H}u_E(x) = Eu_E(x)$$

  - Important: the solution can have a continuous or a discrete spectrum!
  - Discrete spectrum means

    $$E = E_n \qquad \text{with} \qquad n = 1, 2, 3, ...$$

    and

    $$u(x) = u_n(x) \qquad \text{with} \qquad n = 1, 2, 3, ...$$

Review of Quantum Mechanics I

- <u>The Time-Dependent Schrödinger Equation</u>
  - In general we can have both, discrete and continuous eigenvalues.
  - The general solution has the form

$$\Psi(x,t) = \underbrace{\sum_n C_n u_n(x) e^{iE_n t/\hbar}}_{\text{Discrete contribution}} + \underbrace{\int dE\, C(E) u_E(x) e^{iEt/\hbar}}_{\text{Continuous contribution}}.$$

  - Note, some books use the following symbol if it is unknown whether we have discrete, continuous, or combined spectra:

$$\sum\!\!\!\!\!\!\!\int$$