Review of Quantum Mechanics I

- The Commutation Relation
  - 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

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

  - 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

- The Time-Dependent Schrödinger Equation
  - Therefore, we find

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

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

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

  - The second equation is the time-independent Schrödinger equation

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

  - Alternatively, we can write this equation as the eigenvalue equation

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

Review of Quantum Mechanics I

- The Time-Dependent Schrödinger Equation
  - The solution of

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

    provides the eigenvalues *E* as well as the eigenfunctions $u_E(x)$.
  - Important: the solution can have a continuous or a discrete spectrum!
  - Discrete spectrum means

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

    and

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

  - The general solution has the form

    $$\Psi(x,t) = \sum_n C_n u_n(x) e^{-iE_n t/\hbar} + \int dE\, C(E) u_E(x) e^{-iEt/\hbar}.$$

Review of Quantum Mechanics I

- <u>The Expansion Postulate and its Physical Interpretation</u>
  - Consider <u>discrete eigenvalues</u> and functions

$$u_n(x) \qquad \text{and} \qquad E_n.$$

  - The general solution to a given problem is then

$$\Psi(x,t) = \sum_n C_n u_n(x) e^{iE_n t/\hbar}.$$

  - Consider this for the initial time *t=0*

$$\Psi_0(x) = \sum_n C_n u_n(x).$$

Expansion coefficients

  - Multiplying this by $u_m^*(x)$ and integrating over all *x* yields

$$\int dx\ \Psi_0(x) u_m^*(x) = \sum_n C_n \int dx\ u_n(x) u_m^*(x).$$

Review of Quantum Mechanics I

- The Expansion Postulate and its Physical Interpretation
  - Assuming that the eigenfunctions are orthonormal means

$$\int dx\ u_n(x)u_m^*(x) = \delta_{nm}.$$

Kronecker delta

  - Therefore we obtain

$$\int dx\ \Psi_0(x)u_m^*(x) = \sum_n C_n \int dx\ u_n(x)u_m^*(x) = \sum_n C_n\delta_{nm}.$$

  - Thus, the expansion coefficients C_n are given by

$$C_n = \int dx\ \Psi_0(x)u_n^*(x).$$

  - What is the physical meaning of the expansion coefficients C_n?

Review of Quantum Mechanics I

- The Expansion Postulate and its Physical Interpretation
  - In order to answer this question, we calculate the expectation value of the Hamiltonian operator.
  - Assume the physical system is described by the wave function *Ψ(x)*.
  - Therefore, we have

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

Arbitrary (but time-independent) wave function

  - For the wave function *Ψ(x)* we can use the expansion

$$\Psi(x) = \sum_n C_n u_n(x)$$

to derive

$$\langle \hat{H} \rangle = \int dx\ \Psi^*(x) \hat{H} \sum_n C_n u_n(x) = \sum_n C_n \int dx\ \Psi^*(x) \hat{H} u_n(x).$$

Review of Quantum Mechanics I

- The Expansion Postulate and its Physical Interpretation
  - We found

$$\langle \hat{H} \rangle = \sum_n C_n \int dx\ \Psi^*(x) \underbrace{\hat{H} u_n(x)}.$$

  - However, the eigenfunctions $u_n(x)$ satisfy the eigenvalue equation

$$\underbrace{\hat{H} u_n(x)} = E_n u_n(x).$$

  - Using this above yields

$$\langle \hat{H} \rangle = \sum_n C_n \int dx\ \Psi^*(x) E_n u_n(x) = \sum_n C_n E_n \underbrace{\int dx\ \Psi^*(x) u_n(x)}.$$

  - For the expansion coefficients we derived before

$$C_n = \int dx\ \Psi(x) u_n^*(x) \qquad \Rightarrow \qquad C_n^* = \int dx\ \Psi^*(x) u_n(x).$$

Review of Quantum Mechanics I

➢ The Expansion Postulate and its Physical Interpretation

- We finally find

$$\langle \hat{H} \rangle = \sum_n E_n C_n C_n^* = \sum_n E_n \left| C_n \right|^2 .$$

- Furthermore, we can use normalization to find

$$\begin{aligned} 1 &= \int dx \; \Psi^*(x)\Psi(x) = \int dx \; \Psi^* \sum_n C_n u_n(x) \\ &= \sum_n C_n \int dx \; \Psi^* u_n(x) = \sum_n C_n C_n^* \\ &= \sum_n \left| C_n \right|^2 . \end{aligned}$$

Review of Quantum Mechanics I

- The Expansion Postulate and its Physical Interpretation
  - We found

$$\langle \hat{H} \rangle = \sum_n E_n |C_n|^2 \qquad \text{and} \qquad \sum_n |C_n|^2 = 1.$$

  - Note: an energy measurement can only yield one of the eigenvalues E_n.
  - We conclude: $|C_n|^2$ has to be interpreted as the probability that a measurement of the energy for the state $\Psi(x)$ yields the eigenvalue E_n.
  - Assume that we make a measurement and find the result E_n.
  - A repetition of the measurement must yield the same result. Otherwise, how else could we check that the measurement was carried out correctly?

Review of Quantum Mechanics I

- The Expansion Postulate and its Physical Interpretation
  - This, however, means that after the first measurement the system had to be in the eigenstate $u_n(x)$, since that is the only way to ensure that the second measurement will give E_n with certainty.
  - This implies that a measurement projects the initial state into an eigenstate of the observable that is being measured (in our case the energy).
  - The conclusion we found here holds for general systems in which there is a potential energy $V(x)$ and also for observables other than the energy.
  - Examples for other observables are momentum and angular momentum (see later in this course).

Review of Quantum Mechanics I

- Degeneracy
  - Soving an eigenvalue problem means that we compute the energy eigenvalues E_n and the corresponding eigenfunctions $u_n(x)$.
  - There may be more than one eigenfunction that corresponds to the same eigenvalue of a Hermitian operator.
  - Example: $E_1 = E_2$ but $u_1 \neq u_2$.
  - When this occurs, we have a degeneracy.
  - In some cases this has important implications (see, e.g., perturbation theory).

Review of Quantum Mechanics I

- Parity
  - Even eigenfunctions have the property

$$\Psi(x) = \Psi(-x).$$

  - Odd eigenfunctions, on the other hand, satisfy

$$\Psi(x) = -\Psi(-x).$$

  - An arbitrary function can always be written as a sum of an even and an odd function

$$\Psi(x) = \underbrace{\frac{1}{2}\left[\Psi(x) + \Psi(-x)\right]}_{\text{even function}} + \underbrace{\frac{1}{2}\left[\Psi(x) - \Psi(-x)\right]}_{\text{odd function}}.$$

  - Define the parity operator $\hat{P}$ via

$$\hat{P}\Psi(x) = \Psi(-x).$$

Review of Quantum Mechanics I

- Parity
  - Eigenvalue equation for the parity operator
  $$\hat{P}\Psi(x) = \lambda\Psi(x).$$
  - Employing this operator twice yields
  $$\hat{P}^2\Psi(x) = \lambda^2\Psi(x) = \Psi(x).$$
  - Therefore, there are two eigenvalues
  $$\lambda^2 = 1 \qquad \Rightarrow \qquad \lambda = \pm 1.$$
  - The eigenvalues with λ=-1 correspond to
  $$\hat{P}\Psi(x) = \Psi(-x) = \lambda\Psi(x) = -\Psi(x).$$
  odd function
  - The eigenvalues with λ=+1 correspond to
  $$\hat{P}\Psi(x) = \Psi(-x) = \lambda\Psi(x) = \Psi(x).$$
  even function

Review of Quantum Mechanics I

➢ One-Dimensional Problems

- We consider potentials of the form

$$V\left(\vec{r},t\right) = V\left(x\right).$$

- The corresponding Schrödinger equation is in this case

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

- This is an Ordinary Differential Equation (ODE)!
- Depending on the problem, you need to think about conditions which are satisfied (or not):
    - Normalization in the case of bound states.
    - Flux conservation in the case of scattering problems.
    - Continuity of the wave function and its first derivative if there are jumps in the potential.

Review of Quantum Mechanics I

- One-Dimensional Problems
  - Examples for one-dimensional problems:
    - The potential step (Gasiorowicz **4-1**).
    - The potential well (Gasiorowicz **4-2**).
    - The potential barrier (Gasiorowicz **4-3**).
    - Delta function potentials (Gasiorowicz **4-6**).
    - The harmonic oscillator (Gasiorowicz **4-7**).

Not part of this review

I will review this as an example!

Review of Quantum Mechanics I

- <u>One-Dimensional Problems</u>

  - For the <u>harmonic oscillator</u> the time-independent Schrödinger equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2u(x)}{dx^2}+\underbrace{\frac{1}{2}m\omega^2x^2}_{\text{Harmonic oscillator potential}}u(x)=Eu(x).$$

  - Note that at this point ω is just a constant in the potential function.
  - In order to solve this ODE we employ the transformations

$$E=\frac{1}{2}\hbar\omega\epsilon \qquad \text{and} \qquad y=\sqrt{\frac{m\omega}{\hbar}}x.$$

  - Using this in Schrödinger's equation yields ...

Review of Quantum Mechanics I

- <u>One-Dimensional Problems</u>
  - Using this in Schrödinger's equation yields

$$\frac{d^2u(y)}{dy^2} + \left(\epsilon - y^2\right) u(y) = 0.$$

  - First we consider the asymptotic limit $y \rightarrow \pm\infty$. In this limit our ODE simplifies to

$$\frac{d^2u}{dy^2} = y^2 u.$$

  - We try to solve this via

$$u(y) = u_0 e^{-\frac{1}{2}y^2}.$$

  - We find for the derivatives

$$u' = -y u_0 e^{-\frac{1}{2}y^2} \qquad \text{and} \qquad u'' = -u_0 e^{-\frac{1}{2}y^2} + y^2 u_0 e^{-\frac{1}{2}y^2}.$$

Review of Quantum Mechanics I

- <u>One-Dimensional Problems</u>
  - We found

$$u'' = -u_0 e^{-\frac{1}{2}y^2} + y^2 u_0 e^{-\frac{1}{2}y^2}.$$

  - In the considered limit $y \to \pm\infty$, this becomes

$$u'' \approx y^2 u_0 e^{-\frac{1}{2}y^2} = y^2 u.$$

  - We found an asymptotic solution of our ODE!
  - To find the general solution we try the *ansatz*

$$u(y) = h(y) e^{-\frac{1}{2}y^2}.$$

  - The corresponding derivatives are (just use product rule)

$$\begin{aligned} u' &= h' e^{-\frac{1}{2}y^2} - hy e^{-\frac{1}{2}y^2} \\ u'' &= h'' e^{-\frac{1}{2}y^2} - 2h' y e^{-\frac{1}{2}y^2} - h e^{-\frac{1}{2}y^2} + h y^2 e^{-\frac{1}{2}y^2}. \end{aligned}$$

Review of Quantum Mechanics I

- <u>One-Dimensional Problems</u>
  - Using

$$u'' = h''e^{-\frac{1}{2}y^2} - 2h'ye^{-\frac{1}{2}y^2} - he^{-\frac{1}{2}y^2} + hy^2e^{-\frac{1}{2}y^2}$$

in our ODE

$$u'' + \left(\epsilon - y^2\right)u = 0$$

yields

$$\begin{aligned} & h''e^{-\frac{1}{2}y^2} - 2h'ye^{-\frac{1}{2}y^2} - he^{-\frac{1}{2}y^2} \\ + \quad & hy^2e^{-\frac{1}{2}y^2} + \left(\epsilon - y^2\right)he^{-\frac{1}{2}y^2} = 0. \end{aligned}$$

  - Furthermore, we can cancel the exponentials to find

$$h'' - 2yh' + (\epsilon - 1)h = 0.$$

  - This is called the <u>Hermite differential equation</u> (named after Charles Hermite).

Review of Quantum Mechanics I

- One-Dimensional Problems
  - We found the Hermite differential equation

$$h'' - 2yh' + (\epsilon - 1)h = 0.$$

  - The solutions are the Hermite polynomials $H_n(y)$ with the integer number

$$n = \frac{1}{2}(\epsilon - 1).$$

  - For the energy eigenvalues we derive the discrete spectrum

$$E_n = \frac{1}{2}\hbar\omega\,(2n+1) = \hbar\omega\left(n + \frac{1}{2}\right) \qquad \text{with} \qquad n = 0, 1, 2, \ldots$$

  - The eigenfunctions are given by

$$u_n(y) = C_n H_n(y) e^{-\frac{1}{2}y^2} \qquad \text{with} \qquad y = \sqrt{\frac{m\omega}{\hbar}}x.$$

Review of Quantum Mechanics I

- <u>One-Dimensional Problems</u>
  - Note, the Hermite polynomials $H_n(y)$ can be obtained from tables (see, e.g., *https://en.wikipedia.org/wiki/Hermite_polynomials*):

$$H_0(x) = 1,$$
$$H_1(x) = 2x,$$
$$H_2(x) = 4x^2 - 2,$$
$$H_3(x) = 8x^3 - 12x,$$
$$H_4(x) = 16x^4 - 48x^2 + 12,$$
$$H_5(x) = 32x^5 - 160x^3 + 120x,$$
$$H_6(x) = 64x^6 - 480x^4 + 720x^2 - 120$$

  - Some important properties are (see, e.g., Abramowitz & Stegun):

$$H_{n+1} - 2yH_n + 2nH_{n-1} = 0,$$

$$H_{n+1} + \frac{dH_n}{dy} - 2yH_n = 0.$$

Review of Quantum Mechanics I

- One-Dimensional Problems
  - Also very important is the orthogonality relation

$$\int_{-\infty}^{+\infty} dy\ H_n(y) H_m(y) e^{-y^2} = 2^n \sqrt{\pi} n! \delta_{nm}.$$

  - The orthogonality relation and the aforementioned recurrence relations are useful in order to compute expectation values.
  - Plot of some Hermite polynomials (from *https://en.wikipedia.org/wiki/Hermite_polynomials*):