# Chapter 2

# The Formulation of Wave Mechanics

## 2.1 The Schrödinger Equation

□ We have discussed basic properties of wave functions. Now we would like to find an equation of motion (a "wave equation") whose solution for a given problem is the correct wave function.
□ From the discussions of the last chapter some properties of this wave equation are immediately clear. The equation has to be

- linear — so the superposition principle applies.
- homogeneous — so that the normalization of its solutions is not fixed and we can renormalize any solution $\psi$ such that $|\psi|^2$ is a probability density.
- first order in time — since at least for free particles we have established that $\psi(\vec{r}, 0)$ uniquely determines $\psi(\vec{r}, t)$ at any time $t$.

### 2.1.1 Free Particles

□ For free particles the wave equation has to reproduce the dispersion relation $\omega = \hbar k^2/(2m)$ for plane wave solutions. The simplest differential equation to achieve this with the three properties mentioned above is

$$\boxed{-i\hbar\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m}\triangle\psi}\,. \tag{2.1}$$

Here $\triangle = \nabla \cdot \nabla$ is the Laplace operator. Proof: This is readily confirmed by plugging in plane wave solutions.
□ This equation is called the free (time-dependent) Schrödinger Equation. It is of "diffusion type" except for the imaginary unit appearing in it, which makes its solutions manifestly complex valued.
□ We could extend this equation to the general case of particles in a potential $V(\vec{r}, t)$ by postulating a more general dispersion relation

$$\hbar\omega = \frac{\hbar^2}{2m}k^2 + V\,. \tag{2.2}$$

However we will take a different route that will allow us to make explicitly contact with classical mechanics.

### 2.1.2 Action Waves and Hamilton-Jacobi Theory

□ On the outset the wave functions we have postulated to describe particles do not at all resemble classical mechanics with its well-defined motions. We can turn around this question and ask whether there is a formulation of classical mechanics which is based on waves. This is of course the case. In fact the Hamilton-Jacobi theory of classical mechanics is well established. In this subsection we give a brief review. More details can be found in [5] or any good mechanics book.

□ Recall that

$$\boxed{\frac{\partial S}{\partial t} + H(q,p,t) = 0} \tag{2.3}$$

with $p_i = \partial S/\partial q_i$, $i = 1, \dots s$, is a non-linear, first order partial differential equation for the action variable $S(q,t)$ of a mechanical system with $s$ generalized coordinates $q = (q_i)_{i=1}^s$. To be more precise, $S$ is the action with variable endpoint

$$S(q,t) = \int_{t_0}^{t} L(\tilde{q}, \dot{\tilde{q}}, \tilde{t}) d\tilde{t} \tag{2.4}$$

and fixed initial time $t_0$ where $q = \tilde{q}(t)$ is the final point of the motion $\tilde{q}$ at a final time $t$ and $L$ is the Lagrange function of the system. As usual

$$H(q,p,t) = \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L(q,\dot{q},t) \tag{2.5}$$

is the classical Hamilton function of the system.

□ Recall, for systems with constant energy $E$ we can separate the time $t$ from the coordinates $q$ in the action as

$$S(q,t) = W(q) - Et\,. \tag{2.6}$$

From now on we look at a single particle in $\mathbb{R}^3$ in cartesian coordinates and $q = \vec{r}$. The spatial part of the action defines hypersurfaces in coordinate space through the condition $W(q)$ =const. $S = W - Et$ =const. then defines the motion of these hypersurfaces through coordinate space. These moving wave fronts are called action waves.[1]

□ Recall that the velocity of the action wave is

$$\vec{u} = \frac{E}{p}\hat{p} \tag{2.7}$$

where $E$ is the particle energy and $\vec{p} = \nabla S = \nabla W$ is the momentum vector. Obviously this is different from the particle velocity $\vec{v} = \vec{p}/m$, but in fact this is the same expression as the phase velocity of a wave packet of free particles with the same "average" momentum $\vec{p}$. This is our first lead. The classcial action $S$ could be related to the phase of a wave function $\psi$.

□ Recall that $S(q,t)$ has all the information about a classical system. As a very simple example we solve here the problem for a free particle in 1-D. The Hamilton-Jacobi equation in that case is

$$\frac{1}{2m}\left(\frac{\partial S}{\partial x}\right)^2 = -\frac{\partial S}{\partial t}\,. \tag{2.8}$$

[1] Recall that these "waves" often do not resemble our intuitive picture of an oscillating wave. E.g. for a free particle simply $S = \vec{r}\cdot\vec{p} - Et$.

A separation ansatz with $S = W(x) - Et$ gives

$$\left(\frac{\partial W}{\partial x}\right)^2 = \alpha^2 = \text{const.} \tag{2.9}$$

$$-2mE = \alpha^2 \tag{2.10}$$

with a constant $\alpha$ which (from the last equation) can obviously be chosen to be the momentum $p$ of the particle. From the first equation we get

$$S = px - \frac{p^2}{2m}t + \text{const.} \tag{2.11}$$

We can solve for the motion by imposing $\partial S/\partial\alpha = \beta = \text{const.}$ which implies

$$q = \frac{p}{m}t + \text{const.} \tag{2.12}$$

and the last constant can be fixed by the initial condition for $x$.

□ Without further proof we generalize the result to free particles in 3-D. The action in this case is

$$\boxed{S = \vec{p}\cdot\vec{r} - Et}\,. \tag{2.13}$$

Hence we could write the plane wave for the same particles in quantum mechanics as

$$e^{i(\vec{k}\cdot\vec{r}-\omega t)} = e^{\frac{i}{\hbar}S(\vec{r},t)}\,. \tag{2.14}$$

□ As a result of our considerations we postulate that the equation of motion of quantum mechanics should reduce in a suitable limit (the "classical limit") to the Hamilton-Jacobi equation for the phase $S$. We will see that this leads to the correct Schrödinger Equation, and in fact this limit corresponds to the eikonal approximation of wave optics which yields geometric optics.

### 2.1.3 Constraints from the Probabilistic Interpretation

□ For a conserved quantity with spatial density $\rho(\vec{r},t)$ the conservation law

$$\int_V \rho\, d^3r = \text{const.} \tag{2.15}$$

for a co-moving volume $V$ implies the general conservation law

$$\boxed{\frac{\partial\rho}{\partial t} + \nabla\vec{j} = 0} \tag{2.16}$$

where $\vec{j}$ is a suitably defined *current density* associated with $\rho$. (2.16) is called the *continuity equation.*

□ If $\rho$ is a density associated with a distribution of particles (or of particular properties of particles like electric charge), and if those particles move collectively, i.e. described by a common velocity field $\vec{v}(\vec{r},t)$ (e.g. electrons in a wire following the electric field), then the current density is

$$\vec{j} = \rho\vec{v}\,. \tag{2.17}$$

The electric current density associated with the electric charge density is a well known example.
□ In the previous case the continuity equation can be rewritten in an obvious way as

$$\boxed{\frac{\partial \rho}{\partial t} + \rho \nabla \vec{v} + (\nabla \rho) \cdot \vec{v} = 0}\,. \tag{2.18}$$

□ In order to secure a probabilistic interpretation of quantum mechanics we postulate that the equation of motion of quantum mechanics should permit the existence of a current $\vec{j}$ associated with the wave function $\psi(\vec{r}, t)$ such that the continuity equation (2.16) holds for $\rho = |\psi|^2$. Moreover, in the classical limit it should reproduce (2.18) for the collective classical motion of particles.

### 2.1.4 Derivation of the Schrödinger Equation

□ Equipped with these two additional postulates we proceed to a deduction of the equation of motion. The general ansatz for a linear, homogeneous, first order in time wave equation is

$$\left[a + b\frac{\partial}{\partial t} + b_k \frac{\partial}{\partial r_k} + c_{0k}\frac{\partial^2}{\partial t \partial r_k} + c_{jk}\frac{\partial^2}{\partial r_j \partial r_k} + \ldots\right]\psi = 0\,. \tag{2.19}$$

We will not consider higher order terms since we would like to obtain the simplest wave equation that satisfies our postulates.[2] We will also drop the mixed term from the outset, $c_{0k} = 0$, to shorten the derivation which would explicitly demonstrate that they vanish. We write all unknown coefficients explicitly with their real and imaginary parts as

$$a = a' + ia'' \qquad b_0 = b_0' + ib_0'' \quad \ldots \tag{2.20}$$

where all primed coefficients are now real.
□ We can decompose any wave function that is a solution to our ansatz in terms of real-valued amplitude $A(\vec{r}, t)$ and real-valued phase $S(\vec{r}, t)$ as

$$\psi(\vec{r}, t) = A(\vec{r}, t) e^{\frac{i}{\hbar} S(\vec{r}, t)}\,. \tag{2.21}$$

When we plug this expression into the ansatz we obtain the condition

$$\begin{aligned} a + \frac{i}{\hbar} b_0 \frac{pdS}{\partial t} + b_0 \frac{1}{A}\frac{\partial A}{\partial t} + \frac{i}{\hbar} b_k \frac{\partial S}{\partial r_k} + b_k \frac{1}{A}\frac{\partial A}{\partial r_k} \\ + \frac{i}{\hbar} c_{jk}\frac{\partial^2 S}{\partial r_j \partial r_k} - \frac{1}{\hbar^2} c_{jk}\frac{\partial S}{\partial r_j}\frac{\partial S}{\partial r_k} + \frac{2i}{\hbar} c_{jk}\frac{1}{A}\frac{\partial A}{\partial r_j}\frac{\partial S}{\partial r_k} + c_{jk}\frac{1}{A}\frac{\partial^2}{\partial r_j \partial r_k} = 0 \end{aligned} \tag{2.22}$$

where we have used that the coefficients $c_{jk}$ can be chosen symmetric in the indices $j, k = 1, 2, 3$. Separating the real and imaginary part of this equation we arrive at two separate equations

$$\begin{aligned} a' + b_0' \frac{1}{A}\frac{\partial A}{\partial t} + b_k' \frac{1}{A}\frac{\partial A}{\partial r_k} + c_{jk}' \frac{\partial^2 A}{\partial r_j \partial r_k} - \frac{2}{\hbar} c_{jk}'' \frac{1}{A}\frac{\partial A}{\partial r_j}\frac{\partial S}{\partial r_k} \\ - \frac{1}{\hbar} b_0'' \frac{\partial S}{\partial t} - \frac{1}{\hbar} b_k'' \frac{\partial S}{\partial r_k} - \frac{1}{\hbar} c_{jk}'' \frac{\partial^2 S}{\partial r_j \partial r_k} - \frac{1}{\hbar^2} c_{jk}' \frac{\partial S}{\partial r_j}\frac{\partial S}{\partial r_k} = 0 \end{aligned} \tag{2.23}$$

[2] For the first time we have used Einstein's convention to sum over indices occurring twice for brevity. We will use it occasionally througout the manuscript.

and

$$a'' + \frac{1}{\hbar} b_0' \frac{\partial S}{\partial t} + \frac{1}{\hbar} b_k' \frac{\partial S}{\partial r_k} + \frac{1}{\hbar} c_{jk}' \frac{\partial^2 S}{\partial r_j \partial r_k} - \frac{1}{\hbar^2} c_{jk}'' \frac{\partial S}{\vec{p} r_j \partial r_k} + \frac{2}{\hbar} c_{jk}' \frac{\partial A}{\partial r_j}$$
$$\frac{\partial S}{\partial r_k} + b_0'' \frac{1}{A} \frac{\partial A}{\partial t} + b_k'' \frac{1}{A} \frac{\partial A}{\partial r_k} + c_{jk}'' \frac{1}{A} \frac{\partial^2 A}{\partial r_j \partial r_k} = 0 \,. \quad (2.24)$$

□ The Hamilton-Jacobi equation for a particle of mass $m$ in a real-valued[3] potential $V(\vec{r}, t)$ is

$$\frac{\partial S_{\rm cl}}{\partial t} + \frac{1}{2m} \frac{\partial S_{\rm cl}}{\partial r_j} \frac{\partial S_{\rm cl}}{\partial r_j} + V = 0 \quad (2.25)$$

where we denote the classical action as $S_{\rm cl}$ to distinguish it from the phase $S$. If we postulate that this equation for $S_{\rm cl}$ should be compatible with Eq. (2.23) for $S$ in the case $S \to S_{\rm cl}$ the *simplest* solution forces the following choices for coefficients:

$$a' = V \qquad b_0' = 0 \qquad b_k' = 0 \quad (2.26)$$

$$b_0'' = -\hbar \qquad b_k'' = 0 \qquad c_{jk}' = -\frac{\hbar^2}{2m} \delta_{jk} \quad (2.27)$$

$$c_{jk}'' = 0 \quad (2.28)$$

These choices simplify Eq. (2.23) to

$$\frac{\partial S}{\partial t} + \frac{1}{2m} \left[ (\nabla S)^2 - \hbar^2 \frac{\triangle A}{A} \right] + V = 0 \quad (2.29)$$

Note that this is still a full quantum equation. If compared to Hamilton-Jacobi it has an additional term of order $\hbar^2$ which can not be removed by choice of coefficient. However, in the limit $\hbar \to 0$ it is precisely the Hamilton-Jacobi equation and *in that same limit* we can identify $S \to S_{\rm cl}$.

□ Let us briefly look at the classical limit in more detail. In that limit we can identify the gradient of the phase $S$ with particle momentum $\vec{p}$, $\nabla S \to \nabla S_{\rm cl} = \vec{p}$. Thus we can neglect the $\hbar^2$ term if

$$p^2 \gg \hbar^2 \frac{\triangle A}{A} \quad \text{or} \quad \frac{\lambda^2 \triangle A}{A} \ll (2\pi)^2 \,. \quad (2.30)$$

In other words, variations of $A = |\psi|$ have to be small on length scales of the de Broglie wave length $\lambda$ of the particle.

□ Using the set of coefficients we found so far with the second equation (2.24) simplifies it to

$$-\frac{A}{\hbar} a'' + \frac{A}{2m} \triangle S + \frac{1}{m} \nabla A \cdot \nabla S + \frac{\partial A}{\partial t} = 0 \quad (2.31)$$

where we have also multiplied with $A/\hbar$. On the other hand, the continuity equation (2.18) for a classical system with density $\rho = A^2$ with a velocity field given by $\vec{p}/m$ would be

$$2A \frac{\partial A}{\partial t} + \frac{2}{m} A \nabla A \cdot \vec{p} + A^2 \nabla \vec{p} = 0 \,. \quad (2.32)$$

These two equations match in the classical limit $\nabla S \to \nabla S_{\rm cl} = \vec{p}$ if the last free coefficient $a'' = 0$ vanishes.

[3] We comment on complex-valued potentials below.

□ When we plug all coefficients into the original ansatz for the wave equation we obtain

$$\boxed{i\hbar\frac{\partial}{\partial t}\psi = \left(-\frac{\hbar^2}{2m}\triangle + V\right)\psi} \tag{2.33}$$

This is a generalization of the free-particle equation from the beginning of this section and it is called the (time-dependent) Schrödinger equation for particles in real potentials.
□ To summarize, we have ensured that the Schrödinger Equation in the classical limit $\hbar \to 0$, $S \to S_{\rm cl}$ recovers the Hamilton-Jacobi equation and the classical continuity equation.
□ Complex-valued potentials are often used in quantum mechanics. The imaginary part describes particle absorption or creation and thus the continuity equation has to be modified accordingly to contain sink or source terms. We will not discuss this in more detail here.
□ Instead of our decomposition of the wave function into a real-valued phase and amplitude one can absorbe the entire space and time dependence into a complex-valued phase or "quantum action" $S_{\rm qu}$:

$$\psi(\vec{r},t) = Ce^{\frac{i}{\hbar}S_{\rm qu}(\vec{r},t)}\,. \tag{2.34}$$

One can check that the quantum action satisfies a "quantum" version of the Hamilton-Jacobi equation

$$\frac{\partial S_{\rm qu}}{\partial t} + \frac{1}{2m}\left[(\nabla S_{\rm qu})^2 - i\hbar\triangle S_{\rm qu}\right] + V = 0\,. \tag{2.35}$$

Since we will not make much use of this equation here we skip the proof which is straight forward.

### 2.1.5 Momentum Space Representation

□ Analogous to the case of free particle wave functions we can introduce the Fourier transformation $\phi(\vec{k},t)$ for any wave function $\psi(\vec{r},t)$ for which the relevant integrals exist. It will be more convenient to express the momentum space wave function in terms of $\vec{p} = \hbar\vec{k}$. It is customary to introduce a rescaling $\phi(\vec{k},t) \leftrightarrow \hbar^{3/2}\phi(\vec{p},t)$ which with $d^3p = \hbar^3 d^3k$ gives us the following final transformation laws between coordinate and momentum space wave functions

$$\boxed{\begin{aligned}\psi(\vec{r},t) &= \frac{1}{(2\pi\hbar)^{3/2}}\int_{\mathbb{R}^3}\phi(\vec{p},t)e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}d^3p &(2.36)\\ \phi(\vec{p},t) &= \frac{1}{(2\pi\hbar)^{3/2}}\int_{\mathbb{R}^3}\psi(\vec{r},t)e^{-\frac{i}{\hbar}\vec{p}\cdot\vec{r}}d^3r\,. &(2.37)\end{aligned}}$$

□ Example: For a free particle

$$\phi(\vec{p},t) = \phi(\vec{p},0)e^{-\frac{i}{\hbar}E(\vec{p})t}\,, \tag{2.38}$$

and in particular for a plane wave of momentum $\vec{p}_0$ we have

$$\phi(\vec{p},0) = (2\pi\hbar)^{\frac{3}{2}}\,\delta^{(3)}(\vec{p}-\vec{p}_0)\,. \tag{2.39}$$

This follows directly from the discussion of free particle wave packets in the last chapter.
□ From the Schrödinger Equation in coordinate space we can derive a corresponding equation for the wave function $\phi(\vec{p},t)$ in momentum space. We find

$$\boxed{i\hbar\frac{\partial\phi}{\partial t} = \frac{p^2}{2m}\phi + V\left(i\hbar\nabla_p\right)\phi}\,. \tag{2.40}$$

This is called the *Schrödinger Equation in momentum space*. Here the potential energy in momentum space is defined from $V(\vec{r})$ by formally replacing $r$ by $i\hbar\nabla_p$ in the power series of $V$.[4] Proof: HW.

□ We say that $\psi$ and $\phi$, if related by Fourier transformation, describe the same *state* of the physical system.

## 2.2 Probabilities and Expectation Values

□ By construction solutions $\psi(\vec{r},t)$ of the Schrödinger Equation with $\mathbb{R}$-valued potential lead to probability distributions $\rho(\vec{r},t) = |\psi(\vec{r},t)|^2$ which obey a continuity equation in the classical limit. However even without this limit $\rho$ satisfies the continuity equation $\partial\rho/\partial t + \nabla\vec{j} = 0$ where the *current density* associated with the Schrödinger field is

$$\boxed{\vec{j} = \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right)}. \tag{2.41}$$

Proof: HW. This complicated expression can be understood as the real part of the *momentum vector density* of the field ($-i\hbar\nabla$ is the momentum operator as we will see in the next section) divided by $m$, so something like a *velocity density*. In the classical limit $\vec{j} \to \rho\vec{v}$ where $\vec{v}$ is the classical particle velocity.

□ From the continuity equation for $(\rho, \vec{j})$ it follows that solutions $\psi(\vec{r},t)$ to the Schrödinger Equation have to be *continuous* functions and all of their first derivatives in spatial coordinates $\partial\psi/\partial r_j$ have to be continuous as well, as long as the potential energy function $V(\vec{r},t)$ is a proper function. The latter condition means that $V$ can be discontinuous as a function of spatial coordinates (e.g. the famous square well), but the statement is no longer true for generalized functions like the Dirac $\delta$-function.[5] Proof: HW.

□ From now on we will agree to normalize all square-integrable wave functions to unity. I.e. if $\psi \in L^2(\mathbb{R}^3)$ then it is an acceptable wave function if

$$\int_{\mathbb{R}^3} |\psi(\vec{r},t)|^2 d^3r = 1\,. \tag{2.42}$$

Exceptions to this convention will have to be labelled explicitly. We will deal later with wave functions that are not square integrable (e.g. plane waves). Please note that the continuity equation guarantees that if $\psi$ is normalized for one point in time this normalization stays contant.

□ Then $\rho(\vec{r},t) = |\psi(\vec{r},t)|^2$ can be interpreted as a probability density to find a particle at position $\vec{r}$ at time $t$. $|\psi(\vec{r},t)|^2 d^3r$ is the probability to find a particle in the volume $d^3r$ at position $\vec{r}$.

□ Because of Plancherel's Theorem in the case above the momentum space wave function $\phi$ is then normalized to unity as well and we can then interpret the corresponding density in momentum space $|\phi(\vec{p},t)|^2$ as a probability density to find a particle with momentum $\vec{p}$ at time $t$.

□ With probability densities at hand we can define expectation values of observables in a straight forward fashion. For example, the average position of a particle described by a wave function $\psi(\vec{r},t)$ is

$$\langle\vec{r}\rangle = \int \vec{r}|\psi(\vec{r},t)|^2 d^3r\,, \tag{2.43}$$

[4] We will formally define functions of operators a little bit further on.

[5] We will discuss $\delta$-shaped potentials later on.

and the variance around the average is

$$(\Delta r)^2 = \left\langle (\vec{r} - \langle\vec{r}\rangle)^2 \right\rangle = \int (\vec{r} - \langle\vec{r}\rangle)^2 \, |\psi(\vec{r},t)|^2 d^3r \,. \tag{2.44}$$

The latter is consistent with the width of a wave packet for free particles that we had defined earlier.

□ Generally, for any *observable* quantity $F(\vec{r},t)$ which does not depend explicitly on momentum $\vec{p}$ we can define the expectation value

$$\boxed{\langle F\rangle = \int F(\vec{r},t)|\psi(\vec{r},t)|^2 d^3r}\,. \tag{2.45}$$

Note that expectation values are functions of time $t$. We will discuss the equation of motion of expectation values further ahead. Of course, if the wave function is fully known as a function of time $t$ the time dependence of an expectation value can always be calculated explicitly.

□ Similarly, from the momentum space wave function $\phi(\vec{p},t)$ we can calculate the average momentum

$$\langle\vec{p}\rangle = \int \vec{p}|\phi(\vec{p},t)|^2 d^3p \tag{2.46}$$

or the average kinetic energy

$$\langle T\rangle = \int \frac{p^2}{2m}|\phi(\vec{p},t)|^2 d^3p \tag{2.47}$$

of a particle. Generally for an observable $F(\vec{p},t)$ which does not depend explicitly on position $\vec{r}$ we define

$$\boxed{\langle F\rangle = \int F(\vec{p},t)|\phi(\vec{p},t)|^2 d^3p}\,. \tag{2.48}$$

□ We can express expectation values of observables $F(\vec{r})$ also in momentum space via Fourier transformation. In particular we have

$$\begin{aligned}
\langle\vec{r}\rangle &= \int \psi^*(\vec{r},t)\vec{r}\psi(\vec{r},t)d^3r \\
&= \frac{1}{(2\pi\hbar)^3}\int d^3p d^3p' \int d^3r \phi(\vec{p}',t)e^{-\frac{i}{\hbar}\vec{p}'\cdot\vec{r}}\left[-i\hbar\nabla_p e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}\right]\phi(\vec{p},t) \\
&= \frac{1}{(2\pi\hbar)^3}\int d^3p d^3p' \phi(\vec{p}',t)\left[i\hbar\nabla_p\phi(\vec{p},t)\right]\int d^3r e^{-\frac{i}{\hbar}(\vec{p}'-\vec{p})\cdot\vec{r}} + \text{ boundary terms} \\
&= \frac{1}{(2\pi\hbar)^3}\int d^3p d^3p' \phi(\vec{p}',t)\left[i\hbar\nabla_p\phi(\vec{p},t)\right](2\pi\hbar)^3\delta^{(3)}(\vec{p}'-\vec{p}) \\
&= \int d^3p \phi(\vec{p},t) i\hbar\nabla_p\phi(\vec{p},t)
\end{aligned} \tag{2.49}$$

as long as boundary terms disappear for sufficiently fast falling functions (like $L^2$-functions). We can easily generalize this calculation to obtain a general expression for observables $F(\vec{r})$ whose expectation value we would like to calculate with momentum space wave functions. We replace $\vec{r}$ by its momentum space counterpart[6] and we obtain the formula

$$\langle F\rangle = \int \phi^*(\vec{p},t)F\left(i\hbar\nabla_p\right)\phi(\vec{p},t)d^3p\,. \tag{2.50}$$

[6]Later we will say "the momentum space representation of the position operator".

Completely analogous we have

$$\langle F \rangle = \int \psi^*(\vec{r},t) F\left(-i\hbar\nabla_r\right) \psi(\vec{r},t) d^3r \tag{2.51}$$

for all observables $F(\vec{p})$ in momentum space that we want to calculate with coordinate space wave functions.

□ In classical mechanics all the information on a system is encoded in the position and momentum vectors $\vec{r}$ and $\vec{p}$. Any observable that we can hope to measure should thus be written as a function of both variables $F(\vec{r},\vec{p})$. Our results so far seem to suggest that in that general case

$$\boxed{\begin{aligned} \langle F \rangle &= \int \psi^*(\vec{r},t) F\left(\vec{r}, -i\hbar\nabla_r\right) \psi(\vec{r},t) d^3r \qquad (2.52)\\ &= \int \phi^*(\vec{p},t) F\left(i\hbar\nabla_p, \vec{p}\right) \phi(\vec{p},t) d^3p\,. \qquad (2.53) \end{aligned}}$$

This formula holds but only if pairs of conjugate coordinate and momenta, $(x,p_x)$, $(y,p_y)$, $(z,p_z)$, are separable, i.e. as long as they do not appear in products. Proof: Straight forward follwing the derivation in Eq. (2.49).

□ Let us quickly discuss the case of non-separable coordinate and momentum pairs. The proof will not go through in that case because when we attempt the partial integration to push gradients from the phase factor onto one of the wave function factors there will be other terms onto which the gradient will act, see Eq. (2.49). Of course this goes back to the fact that $x\frac{\partial}{\partial x} \neq \frac{\partial}{\partial x}x$ and hence $xp_x \neq p_x x$ as operators which we will discuss in more detail in the next section. What are the consequences for such observables? It means that expectation values calculated in a naive way in coordinate and momentum space may not coincide which makes their interpretation as a "classical" quantity difficult. We will see in the next section that these observables coincide with those for which there is an ambiguity for assigning a quantum mechanical operator to a well defined classical quantity.

□ Important examples: Angular momentum $\vec{L} = \vec{r} \times \vec{p}$ is an observables which depends both on position and momentum, but conjugate pairs are separable and thus $\vec{L}$ is a "good" (and important!) observable in quantum mechanics. On the other hand, in the classical action $S$ coordinate pairs are non-separable, even in the free case where $S = \vec{r}\cdot\vec{p} - Et$.

## 2.3 Operators and Operator Algebra

### 2.3.1 Spaces of Functions and Operators

□ Mathematically we can organize possible wave functions $\psi$ into spaces of functions. Because the Schrödinger Equation is linear we will be interested in *linear spaces* or *vector spaces* over $\mathbb{C}$. I.e. if $\psi_1$ and $\psi_2$ are in that vector space then $\lambda\psi_1 + \psi_2$ is again in that space for any number $\lambda \in \mathbb{C}$.[7]

□ Examples: $L^1(\mathbb{R}^n)$, $L^2(\mathbb{R}^n)$ and $C^1(\mathbb{R}^n)$, i.e. the spaces of integrable, square-integrable and differentiable (complex-valued) functions over $\mathbb{R}^n$ are examples of vector spaces of functions.

[7] Of course the usual rules expected from a vector space, e.g. commutativity and associativity of the vector sum, etc. apply here.

□ Let $\mathcal{S}_1$ and $\mathcal{S}_2$ be two vector spaces of functions. A mapping $F : \mathcal{S}_1 \to \mathcal{S}_2, f \mapsto g$ is often called an operator in that case. An operator $F$ is called *linear* if $F(\lambda\psi_1 + \psi_2) = \lambda F(\psi_1) + F(\psi_2)$ and it is called *anti-linear* if $F(\lambda\psi_1 + \psi_2) = \lambda^* F(\psi_1) + F(\psi_2)$ for any $\lambda \in \mathbb{C}$ and $\psi_1$, $\psi_2 \in \mathcal{S}_1$.
□ Examples: Multiplicative operations, e.g. $f(x) \mapsto xf(x)$ and derivative operations, e.g. $f(x) \mapsto df/dx$ are important classes of linear operators between suitable functional vector spaces.
□ For $f \in L^2(\mathbb{R}^3)$ and an operator $O$ on that space, i.e. $O : L^2(\mathbb{R}^3) \to L^2(\mathbb{R}^3)$, we define the expectation value of $O$ (in the coordinate space representation) as

$$\boxed{\langle O \rangle = \int_{\mathbb{R}^3} f^*(\vec{r}) O f(\vec{r}) d^3r}. \tag{2.54}$$

□ With this new definition we realize that we can recast our previous definition of expectation values as expectation values of operators if we identify observable quantities with operators on the space of wave functions. We propose the following reinterpretation:

- The physical states of a system can be identified with (normalized) vectors both in a vector space of coordinate space wave functions $\mathcal{S}_r$ and a space of momentum space wave functions $\mathcal{S}_p$. Wave functions in both spaces describing the same state are related by Fourier transformation.
- Physical observables $O$ that depend on position $\vec{r}$ and momentum $\vec{p}$ can be identified with operators $O_r : \mathcal{S}_r \to \mathcal{S}_r$ and $O_p : \mathcal{S}_p \to \mathcal{S}_p$ and the expectation value of $O$ in a state $\psi$ corresponds to the expectation value of either operator,

$$\langle O \rangle = \int_{\mathbb{R}^3} \psi_r^*(\vec{r}) O_r \psi_r(\vec{r}) d^3r = \int_{\mathbb{R}^3} \psi_p^*(\vec{p}) O_p \psi_p(\vec{p}) d^3p \tag{2.55}$$

  as long as pairs of conjugate variables are separable.[8]

□ Identifying observbles with suitable operators is a big step in developing the formalism of quantum mechanics. Here we list some observables for which we have already found or can easily identify operators in coordinate and momentum space representation.

| Classical observable $O$ | Coord. space operator $O_r$ | Mom. space operator $O_p$ |
|---|---|---|
| Position $\vec{r}$ | $\vec{r}$ | $i\hbar\nabla_p$ |
| Momentum $\vec{p}$ | $-i\hbar\nabla_r$ | $\vec{p}$ |
| Angular momentum $\vec{L}$ | $-i\hbar\vec{r} \times \nabla_r$ | $i\hbar\nabla_p \times \vec{r}$ |
| Kinetic energy $T$ | $-\frac{\hbar^2}{2m}\triangle$ | $\frac{p^2}{2m}$ |
| Potential energy $V$ | $V(\vec{r})$ | $V\left(i\hbar\nabla_p\right)$ |
| Energy/Hamilton function $E$ or $H$ | $-\frac{\hbar^2}{2m}\triangle + V(\vec{r})$ | $\frac{p^2}{2m} + V\left(i\hbar\nabla_p\right)$ |

□ With the concept of a Hamilton operator $H$ the Schrödinger Equation in both coordinate and momentum space can be written in elegant short hand notation as

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = H\psi}. \tag{2.56}$$

[8] In the future we will be happy to drop the indices $r$ and $p$ on operators if it is clear or irrelevant which representation is used.

### 2.3.2 Products and Commutators

☐ Two operators $F, G : \mathcal{S} \to \mathcal{S}$ on a space $\mathcal{S}$ can be concatenated in the usual sense by applying them sequentially, creating a new operator $G \circ F$ on $\mathcal{S}$, $G \circ F : \mathcal{S} \to \mathcal{S}$, $f \mapsto G(F(f))$.
☐ We will usually write $GF$ instead of $G \circ F$, but this *operator product* is usually not commutative, i.e. in general $FG \neq GF$. The most important class of examples is the case where one operator is multiplicative involving a coordinate, and the other one contains its derivative, e.g. $x(d/dx) \neq (d/dx)x$ in the operator sense.[9]
☐ It is hence useful to define the *commutator* of two operators $F$, $G$,

$$\boxed{[F, G] = FG - GF}. \tag{2.57}$$

Note that the commutator is again an operator on the same space.
☐ We can establish the following properties for commutators of operators $F$, $G$, $H$ and numbers $\lambda \in \mathbb{C}$:

$$[F, G] = -[G, F] \qquad \text{Anti symmetry} \tag{2.58}$$

$$\begin{aligned} [F, \lambda G + H] &= \lambda[F, G] + [F, H] \\ [\lambda F + G, H] &= \lambda[F, H] + [G, H] \end{aligned} \qquad \text{Bi-linearity} \tag{2.59}$$

$$\begin{aligned} [FG, H] &= F[G, H] + [F, H]G \\ [F, GH] &= [F, G]H + G[F, H] \end{aligned} \qquad \text{Product rule} \tag{2.60}$$

$$[F, [G, H]] + [H, [F, G]] + [G, [H, F]] = 0 \qquad \text{Jacobi Identity} \tag{2.61}$$

Proof: Most of these rules are straight forward. The Jacobi identity will be a HW problem.
☐ The properties established here make the commutator a *Lie product* or *Lie bracket* on the *algebra of operators* over $\mathcal{S}$.
☐ In quantum mechanics, pairs of conjugate variables and momenta are important, just as they are in classical mechanics. Among them position and momentum in cartesian coordinates are particularly interesting. We find

$$[x, p_x] = i\hbar\, \mathbf{Id} \tag{2.62}$$

where $\mathbf{Id}$ is the identity operator of the space of functions. Proof: In coordinate space representation

$$[x, p_x]f = x\left(-i\hbar\frac{\partial}{\partial x}\right)f - \left(-i\hbar\frac{\partial}{\partial x}\right)(xf) = i\hbar f - i\hbar\frac{\partial f}{\partial x} + i\hbar\frac{\partial f}{\partial x} = i\hbar f \tag{2.63}$$

for any test function $f(x)$. We will find the same result if we repeat this calculation is momentum space representation.
☐ Generally we find the following fundamental commutator relations

$$\boxed{[r_j, p_k] = i\hbar\delta_{jk}}, \tag{2.64}$$

$j, k = 1, 2, 3$. We will omit the explicit mentioning of $\mathbf{Id}$ if it is clear that we deal with an operator. Proof: This follows immediately from the previous paragraph.

[9] I.e. applied to test functions to the right.

□ Coordinate and momentum space commutators are consistent with each other. Let $F(\vec{r},\vec{p})$, $G(\vec{r},\vec{p})$ be two observables with separable pairs of conjugate variables. Let $F_r$, $G_r$ be the operators representing them in coordinate space on a space $\mathcal{S}$ of sufficiently fast falling functions, and let $F_p$, $G_p$ be their counterparts in momentum space. Then the commutators in coordinate and momentum space are operators related by Fourier transformation, i.e.

$$[F_r, G_r]\, f(\vec{r}) = \frac{1}{(2\pi\hbar)^{3/2}} \int [F_p, G_p]\, \hat{f}(\vec{p}) e^{\frac{i}{\hbar}\vec{r}\cdot\vec{p}} d^3p \tag{2.65}$$

and vice versa. Here $f$ is a test function in $\mathcal{S}$ and $\hat{f}$ is its Fourier transformation. Proof: HW.
□ In particular, if a commutator is a constant times the identity operator, e.g. $[F_r, G_r] = \alpha\,\mathbf{Id}$, $\alpha \in \mathbb{C}$ then the commutators in coordinate and momentum space are equal. This is e.g. the case for the fundamental commutators between position and momentum.
□ We can define analytic functions of operators by formal power series. For example for any operator $A$ we can define the exponential function as

$$e^A = \mathbf{Id} + A + \frac{1}{2!}A \circ A + \ldots = \sum_{k=0}^{\infty} \frac{1}{k!} A^k\,. \tag{2.66}$$

□ Careful: Since operators usually don't commute many treasured properties of analytic functions are no longer valid or more complicated in the operator case. The most famous example we are going to use is the *Baker-Campbell-Hausdorff Formula*

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]+\frac{1}{12}[A,[A,B]]-\frac{1}{12}[B,[B,A]]-\frac{1}{24}[B,[A,[A,B]]]+\ldots} \tag{2.67}$$

where there is an infinite series of terms with an increasing number of commutators in the exponent. Proof: We will discuss the special case where both $A$ and $B$ commute with $[A, B]$ in the HW.
□ We will discuss a possible analogy between the Poisson bracket of classical mechanics and the commutator a little bit later.
□ Recall that observables with non-separable pairs of conjugate coordinates and momenta are not guaranteed matching expectation values in coordinate and momentum space representation. Now we realize that those cases have further problems. Generally, if two classical quantities $f$, $g$ have non-commuting operator representations $F$, $G$ (say in coordinate space), then it is not clear how to represent the quantity $fg$ as an operator. Since $fg = gf$ classically but $FG \neq GF$ as operators. Thus we have to accept the existence of cases where there is an ambiguity in the mapping of classical quantities to operators. Sometimes linear combinations like $(FG + GF)/2$ seem to be the "right" choice of operator in such cases. We will explore this further in the HW.

## 2.4 The Dynamics of Expectation Values

### 2.4.1 Equation of Motion for Expectation Values

□ We would like expectation values of operators to have a classical interpretation and thus they should follow the classical equations of motion. For example the average position $\langle\vec{r}\rangle$ of a wave packet should represent the position of a particle and thus move approximately classically, and similarly the average momentum $\langle\vec{p}\rangle$ of a wave packet should correspond to our intuitive understanding of the momentum of a particle.

□ Let $F$ be an operator and $\psi(\vec{r},t)$ be a sufficiently fast falling solution of a Schrödinger Equation with mass $m$ and potential energy $V(\vec{r})$. Then we find the equation of motion for the expectation value of $F$ with respect to $\psi$ is

$$\boxed{i\hbar\frac{d}{dt}\langle F\rangle = \langle[F,H]\rangle + i\hbar\left\langle\frac{\partial F}{\partial t}\right\rangle}. \tag{2.68}$$

Proof: Applying the Schrödinger Equation we find

$$\begin{aligned} i\hbar\frac{d}{dt}\langle F\rangle &= i\hbar\int\psi^* F\frac{\partial\psi}{\partial t}d^3r + i\hbar\int\psi^*\frac{\partial F}{\partial t}\psi d^3r + i\hbar\int\frac{\partial\psi^*}{\partial t}F\psi d^3r \\ &= \int\psi^* FH\psi d^3r - \int(H\psi)^* F\psi d^3r + i\hbar\left\langle\frac{\partial F}{\partial t}\right\rangle \\ &= \langle FH\rangle - \int\left(-\frac{\hbar}{2m}\right)\triangle\psi^* F\psi d^3r - \langle VF\rangle + i\hbar\left\langle\frac{\partial F}{\partial t}\right\rangle = \langle FH\rangle - \langle HF\rangle + i\hbar\left\langle\frac{\partial F}{\partial t}\right\rangle \end{aligned} \tag{2.69}$$

where the last identity comes from two partial integrations.
□ We note the formal correspondence of this equation with the equation

$$\frac{df}{dt} = \{f,H\} + \frac{\partial f}{\partial t} \tag{2.70}$$

for a classcial quantity $f$ where $\{.,.\}$ is the Poisson bracket (see e.g. [5])[10] and $H$ is the classical Hamilton function. Thus $\langle F\rangle$ moves like the corresponding classical quantity $F_{\rm cl}$ if $\langle[F,H]\rangle \approx i\hbar\{F_{\rm cl},H_{\rm cl}\}$.
□ Comparing commutators of operators and Poisson brackets of their classical counterparts we indeed find in simple cases an even stronger statement, a direct correspondence

$$[F,G] = i\hbar\{F_{\rm cl},G_{\rm cl}\}\,\mathbf{Id}\,. \tag{2.71}$$

However, this *correspondence principle* is *not generally true.* A positive example is the fundamental commutator

$$[r_j,p_k] = i\hbar\delta_{jk} = i\hbar\{r_j,p_k\} \tag{2.72}$$

where $\vec{r}$ and $\vec{p}$ on the right hand side are the classical position and momentum. More examples and counter examples will be discussed in the HW.
□ From the equation of motion for expectation values we find the following corollary if an operator $F$ does not depend explicitly on time. If $F$ commutes with the Hamilton operator $H$, i.e. $[F,H]=0$ then $\langle F\rangle =$ const. for any state $\psi$. In that case we call $F$ an equation of motion in analogy to classical mechanics.
□ Examples:

- $[\vec{p},T]=\vec{0}$, i.e. momentum is a constant of motion for free particles.
- $[\vec{L},T]=\vec{0}$, i.e. angular momentum is a constant of motion for free particles. Proof: HW.
- $[H,H]=0$, i.e. the average energy of a system is conserved as long as $\partial H/\partial t = 0$.

[10] We agree on the convention $\{f,g\} = \sum_k\left(\frac{\partial f}{\partial r_k}\frac{\partial g}{\partial p_k} - \frac{\partial f}{\partial p_k}\frac{\partial g}{\partial r_k}\right)$.

### 2.4.2 The Ehrenfest Theorem

□ In the following we will need the following important commutators:

$$[r_k, H] = i\hbar\frac{p_k}{m} \tag{2.73}$$

$$[p_k, f(\vec{r})] = -i\hbar\nabla f(\vec{r}) \tag{2.74}$$

for $k = 1, 2, 3$ where $f(\vec{r})$ is any differentiable function on $\mathbb{R}^3$. Proof: For the first identity we find $[r_k, H] = [r_k, p^2/(2m)] = [r_k, p_l]p_l/m = i\hbar\delta_{k,l}p_l/m = i\hbar p_k/m$. The second one is straight forward to show.

□ Ehrenfest Theorem: Let $\psi$ be a state solving a Schrödinger Equation for particles of mass $m$ in a potential $V(\vec{r})$. Then we find the following equations of motion for the average position and momentum in the state $\psi$.

$$\boxed{m\frac{\langle\vec{r}\rangle}{dt} = \langle\vec{p}\rangle \ ,} \tag{2.75}$$

$$\boxed{\frac{\langle\vec{p}\rangle}{dt} = \langle F\rangle \ .} \tag{2.76}$$

Here $F = -\nabla V$ is the force associated with the potential energy $V$. Proof: We have $d\langle\vec{r}\rangle/dt = \langle[\vec{r}, H]\rangle/(i\hbar) = \langle\vec{p}\rangle/m$ and $d\langle\vec{p}\rangle/dt = \langle[\vec{p}, H]\rangle/(i\hbar) = \langle-\nabla V\rangle$.

□ Recall the canonical equations from classical mechanics,

$$m\frac{\vec{r}_{\rm cl}}{dt} = \vec{p}_{\rm cl} \, , \tag{2.77}$$

$$\frac{\vec{p}_{\rm cl}}{dt} = -\nabla V\left(\vec{r}_{\rm cl}\right) \ . \tag{2.78}$$

Hence the equations of motion for the expectation values of position and momentum are the same as the equations for their classical counterparts if $\langle\nabla V(\vec{r})\rangle \approx \nabla V\left(\langle\vec{r}\rangle\right)$.

## 2.5 Fundamental Properties of Solutions of the Schrödinger Equation

### 2.5.1 Eigenvalues and Eigenfunctions of Operators

□ Let $F$ be a linear operator[11] on a space $\mathcal{S}$ of functions. If there exists a $\psi \in \mathcal{S}$ and a $\alpha \in \mathbb{C}$ such that

$$\boxed{F\psi = \alpha\psi} \tag{2.79}$$

we call $\alpha$ an *eigenvalue* of $F$ and $\psi$ an *eigenfunction* or *eigenvector* (in the vector space of functions).

□ This is the natural generalization of the concep of eigenvalue and eigenvector from finite-dimensional vector spaces like $\mathbb{R}^n$.

□ If $\psi$ is eigenfunction for $F$ with eigenvalue $\alpha$ then $\lambda\psi$ with any $\lambda \in \mathbb{C}$ is also an eigenfunction. The set of $\lambda\psi$ represent a 1-dimensional subspace of $\mathcal{S}$, the *eigenspace* for $\alpha$.

□ If an operator $F$ has more than one linearly independent eigenvector for a given eigenvalue $\alpha$ we call the eigenvalue degenerate with degeneracy $k$ ($\in \mathbb{N}$) if the largest subspace of $\mathcal{S}$ spanned by eigenfunctions for $\alpha$ has dimension $k$.

[11] All operators from here on will be linear unless explicitly allowed otherwise.