Quantum Mechanics I

R. J. Fries,[1,2]

[1]Cyclotron Institute, Texas A&M University, College Station TX, USA
[2]Department of Physics and Astronomy, Texas A&M University,
College Station TX, USA

February 18, 2015

Contents

Chapter 1

From Classical Mechanics to Wave Mechanics

We have experimental evidence, some of which is briefly mentioned in Sec. I.2.1 below, that the laws of classical mechanics (CM) are insufficient in the microscopic realm. More precisely, we have to replace CM with another theory, *quantum mechanics* (QM), when the classical action S for the motion is comparable to or smaller than a new scale given by Planck's constant h, i.e. if

$$S \lesssim h \,. \tag{1.1}$$

The value of h is

$$h = 6.62606957 \times 10^{-34} \mathrm{m}^2 \mathrm{kg/s} \,. \tag{1.2}$$

Recall that for a free point particle the position and time dependent action is $S = \vec{p} \cdot \vec{x} - Et$ where momentum is $\vec{p}$, position is $\vec{x}$, energy is denoted by E and time is t. The question is whether, say for a bound state, typical values of displacement and momentum are small enough. For example for an electron with kinetic energy equal to 13.6 eV (ionization energy of elemental hydrogen), and for a displacement given by the Bohr radius of 5.3×10^{-11} m we find $|\vec{p}||\vec{x}| = 1.1 \times 10^{-34}$ m^2 kg/s, so atomic physics involves quantum mechanics! We will find a more quantitative argument about what it means to go from quantum mechanics to a *classical limit* in Ch. II.

We will leave in place the constraint from classical mechanics that physical velocities should be much smaller than the speed of light, $|\vec{v}| \ll c$ to avoid relativistic effects.

This manuscript follows quite shamelessly the book by Merzbacher [1], supplemented with elements from other authors, e.g. Fick [2]. For the mathematical background of Hilbert spaces and functional analysis, which is mostly evaded here for time constraints I refer to Fano [3]. There are many more good books on quantum mechanics which the reader can readily find.

1.1 Preview: Axioms of Quantum Mechanics

☐ Recall the axioms of classical mechanics (cf. Arnold, or Fries : Analytical Mechanics).

(A) A particle ("point mass") and its motion are described by a differentiable map $x : \mathbb{R} \to \mathbb{R}^3$, $t \mapsto x(t)$. A system of N particles correspondingly is a map into $\mathbb{R}^{3N}$ by direct product.

(B) Galileo's Principle of Relativity: There exist coordinate systems (called "inertial") with the following properties: (i) All laws of classical mechanics at all moments of time are the same

in all inertial coordinate systems. (ii) All coordinate systems in uniform, rectilinear motion with respect to an inertial one (i.e. connected by transformations of the Galilei group $\mathcal{G}(3,1)$) are themselves inertial.

(C) Newton's Principle of Determinacy: The initial state of a mechanical system, i.e. the totality of positions and velocities of its point masses at some moment in time, *uniquely* determines all of its motion.

In essence classical mechanics is a theory of second order differential equations (or equivalent systems of equations) whose solutions are the "motion", i.e. the maps $x(t)$.

□   We will spend the first half of this course convincing ourselves that in the microscopic world these axioms are superseded by the following set.

(Q1) A system of particles is described by a complex Hilbert space $\mathcal{H}$; composite systems consisting of N subsystems are described by the direct product of the Hilbert spaces of the subsystems. Each possible state of the system is described by a ray (or unit vector) $|\psi\rangle$.

(Q2) Observables, i.e. measurable physical quantities[1], are represented by linear, self-adjoint operators acting on $\mathcal{H}$. The possible outcomes of a measurement of an operator $\mathcal{O}$ are its eigenvalues λ.

(Q3) If a system is in a state $|\psi\rangle$ the probability to measure the eigenvalue λ for an observables $\mathcal{O}$ is $w = |\langle\phi_\lambda|\psi\rangle|^2$ where $|\phi_\lambda\rangle$ is an eigenstate for the eigenvalue λ. After the measurement the system will be in an eigenstate of λ.

(Q4) There is a linear, unitary (projective) representation of the Galilei group $\mathcal{G}(3,1)$ on $\mathcal{H}$ and the laws of quantum mechanics are invariant under Galilei transformations, as long as no measurement is performed on the system.

□   Consistency with classical mechanics. We will find that in quantum mechanics expectation values for positions $\langle x\rangle$ move as a function of time according to the laws of classical mechanics (Ehrenfest Theorem).

1.2   The Case For Matter Waves

1.2.1   Experimental Findings

□   The idea that matter can be described as waves under certain circumstances was established in a series of milestone experiments and their interpretation in the early 20th century. They roughly fall in two categories: discreteness of energy for bound states of matter or of light interacting with such bound states, and interference effects for free particles similar to those of wave optics.

□   Planck's blackbody radiation formula (1900). Assuming that oscillators in a blackbody can only take *quantized* energies

$$E_n = nh\nu \tag{1.3}$$

where $n \in \mathbb{N}$, ν is the frequency and h is a new scale called *Planck's constant*, Planck found that the energy density of the radiation field is

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1} \tag{1.4}$$

---

[1]At least this applies to observables which are explicitly depending on coordinates x or momenta p.

consistent with experimental results. Here T is temperature, c is the speed of light and k is Boltzmann's constant. This is how the existence of a scale h was first postulated. In the limit $h\nu \ll kT$ (i.e. many *quanta* present at a given temperature) we recover the classical result

$$u(\nu, T) \to \frac{8\pi}{c^3} \nu^2 kT \tag{1.5}$$

(Rayleigh's law). Note how h conveniently cancels in the classical limit. We interpret this return to classical physics as a consequence of the fact that "quantization" of energy is unimportant if many quanta are available. On the other hand, in the limit $h\nu \gg kT$ quanta are rare and have large energy (compared to the thermal energy), and this limit is the deep quantum regime of Planck's formula

$$u(\nu, T) \to \frac{8\pi h\nu^3}{c^3} e^{-h\nu/kT} \tag{1.6}$$

(Wien formula).

□   Einstein's explanation of the photoelectric effect (1905): Einstein's idea that electromagnetic waves of frequency ν come in *quanta* of energy

$$\boxed{E = h\nu} \tag{1.7}$$

is another cornerstone of the early days of quantum physics.

□   Stable atomic orbits and atomic spectra (Bohr, 1913), (Bohr and Sommerfeld, 1916): Only certain classical trajectories of electrons are allowed in an atom. They can be determined by Bohr's quantization condition

$$\boxed{\oint p_i dq_i = nh} \tag{1.8}$$

where again $n \in \mathbb{N}$ and q_i, p_i, $i = 1, \ldots, s$ are pairs of conjugate generalized coordinates and momenta. The hydrogen atom will be discussed as a simple example at the end of this subsection. In the Bohr-Sommerfeld model absorbed or emitted electromagnetic waves lead to an increase or decrease, respectively, of the energy of an electron by moving it between discrete levels, leading to discrete series of absorption and emission spectra with allowed frequencies

$$\nu = \frac{1}{h} |E' - E| \tag{1.9}$$

where E and E' are the initial and final energy level. Bohr-Sommerfeld quantization works for a number of simple systems besides the hydrogen atom.

□   Interference and diffraction effects: A direct indication that free particles can behave like waves is found in scattering experiments with slits or periodic lattices (Davisson and Germer, 1927). De Broglie postulated that particles of momentum p resemble plane waves of wave length

$$\boxed{\lambda = \frac{h}{p}}, \tag{1.10}$$

the *de Broglie wave length* of a particle.

□   Preliminary resolution: A particle-wave duality emerges for matter (electrons, protons, atoms, etc.) as well as for electromagnetic radiation ("photons"). Single particles, e.g. sent into a double slit experiment, are still detected as single particles on the other side (instead of a spread out wave). On the other hand a beam of many particles in the same experiment forms an interference

pattern similar to wave optics. We conclude that the *wave aspect* of the particles describes their *statistical distribution.*

□ Example: Bohr-Sommerfeld quantization of circular orbits in the hydrogen atom. We need to analyze phase space trajectories of classical motion in the Kepler problem. In suitable spherical coordinates the kinetic and potential energies for an electron of mass m are

$$T = \frac{1}{2}m\left(\dot{r}^2 + r^2\dot{\phi}^2\right) \quad, \quad U = -\frac{e^2}{4\pi\epsilon_0 r} \tag{1.11}$$

(see e.g. Fries : Analytical Mechanics, or any good mechanics textbook). The Lagrange function and total energy are $L = T - U$ and $E = T + U$ respectively. The conjugate momentum for the azimuthal angle ϕ is

$$p_\phi = \frac{\partial L}{\partial \dot{\phi}} = mr^2\dot{\phi} = L_z \tag{1.12}$$

i.e. it is equal to the angular momentum component perpendicular to the plane of the orbit. The quantization condition for ϕ gives

$$\oint p_\phi d\phi = \int_0^{2\pi} mr^2\dot{\phi} = 2\pi mr^2\dot{\phi} \tag{1.13}$$

which has to be set equal to nh. Hence the angular momentum L_z is quantized in multiples of the modified Planck constant $\hbar$,

$$L_z = n\hbar \quad \text{where} \quad \hbar = \frac{h}{2\pi}. \tag{1.14}$$

From the Lagrange equation for r we find the radial equation of motion

$$m\ddot{r} - mr\dot{\phi}^2 + \frac{e^2}{4\pi\epsilon_0 r^2} = 0 \tag{1.15}$$

For circular motion ($\ddot{r} = 0$) the quantization of L_z (note that the second term is equal to $L_z^2/(mr^3)$) then translates directly into a quantization condition for the radius of the motion

$$r = n^2\frac{4\pi\epsilon_0\hbar^2}{me^2} \tag{1.16}$$

which leads for $n = 1$ to the well known Bohr radius $r_1 = 5.29 \times 10^{-11}$ m if the electron mass is used. The total energy for an orbit with given n can then be calculated to be

$$E = -\frac{1}{n^2}\frac{2\pi^2 me^4}{(4\pi\epsilon_0)^2 h^2} \equiv -\frac{1}{n^2}R_H \tag{1.17}$$

where R_H is called the Rydberg constant. For $n = 1$ we obtain the well known hydrogen ground state binding energy of -13.6 eV. The gaps between the energy levels correspond to the experimentally found series of the hydrogen emission spectrum (Lyman, Balmer, etc.).

1.2.2 The Concept of Wave Functions

☐ Interference and diffraction phenomena lead us to believe that free particles should be described by traveling waves and that de Broglie's equation connects particle momentum and wave length.

☐ Bound particles taking only certain energies are reminiscent of standing waves in classical physics (strings, membranes, etc.). A "quantization" of wave length forced by boundary conditions translates into quantized energies.

☐ Hence we postulate that particles can be described by scalar fields

$$\psi(\vec{r}, t) = \psi(x, y, z, t) \tag{1.18}$$

called the *wave functions* of the particles. These could be real or complex valued which will be clarified below.

☐ The restriction to scalar fields is for simplicity only at this point. Quantum theory allows for fields with internal structure, e.g. spin. Vector fields or spinor fields are allowed and are typically discussed in an advanced quantum course. This means for now we neglect the spin of particles.

☐ ψ itself could be negative or even complex and does not lend itself to a direct probabilistic interpretation. Following the example of electrodynamics, where intensity is the square of the wave field, we postulate that the absolute value square of the wave function

$$\boxed{\rho(\vec{r}, t) = |\psi(\vec{r}, t)|^2} \tag{1.19}$$

is the *probability density* associated with the wave function ψ. ρ is real and positive definite (but might still need to be properly normalized as discussed later). ψ is then sometimes called the *probability amplitude*. Note that for a complex number a we define $|a|^2 = aa^*$ where * is our notation for complex conjugation.

☐ Superposition Principle: In order to exhibit interference effects we need to postulate the superposition principle to hold. If $\psi_1(\vec{r}, t)$ and $\psi_2(\vec{r}, t)$ describe possible physical situations (an amplitude for positions of particles as a function of time) then

$$\psi(\vec{r}, t) = \alpha\psi_1(\vec{r}, t) + \beta\psi_2(\vec{r}, t) \tag{1.20}$$

where α, β are complex numbers, is also a possible physical situation.

☐ Let us consider the double slit experiment as an example. Suppose only one slit is open at a time and a particle going through slit i, $i = 1, 2$ is described by a wave function ψ_i. The intensities are given by $|\psi_i|^2$ respectively. When both slits are open at the same time the wave function is a superposition $\psi_1 + \psi_2$ and (modulo proper normalization) the new probability density is

$$|\psi_1 + \psi_2|^2 \neq |\psi_1|^2 + |\psi_2|^2. \tag{1.21}$$

The additional mixed terms on the left hand side, $\psi_1\psi_2^* + \psi_1^*\psi_2$, are responsible for the interference pattern.

1.3 Plane Waves

☐ Combining the results of the last section and de Broglie's postulate we assume that free particles of momentum $\vec{p}$ are represented by plane waves. Plane waves have a characteristic wave

vector $\vec{k}$ and (angular) frequency ω. Recall the connection with wave length λ and (regular) frequency ν for a plane wave

$$k = \frac{2\pi}{\lambda} \quad , \quad \omega = 2\pi\nu \tag{1.22}$$

where $k = |\vec{k}|$. The direction of $\vec{k}$ gives the direction of propagation of the plane wave and should coincide with the direction of motion of the particle, i.e. $\vec{k} \parallel \vec{p}$. Then from de Broglie we postulate

$$\boxed{\vec{p} = \hbar\vec{k}} \tag{1.23}$$

for plane waves representing free particles.

☐ The most general form of a plane wave of given $\vec{k}$ and ω is

$$\psi(\vec{r}, t) = A\cos\left(\vec{k} \cdot \vec{r} - \omega t\right) + B\sin\left(\vec{k} \cdot \vec{r} - \omega t\right) . \tag{1.24}$$

It is an experimental fact that we do not observe oscillations in intensity for single free particles or beams of particles. In other words, $|\psi|^2$ should actually be translationally invariant for plane waves representing free particles along the direction of propagation. Let us investigate the consequences of a small shift in propagation direction $\vec{\delta} = \epsilon\vec{k}/k^2$, with small positive ϵ, on ψ. We will demand

$$\psi(\vec{r} + \vec{\delta}, t) = a\psi(\vec{r}, t) \tag{1.25}$$

such that a is a pure phase, i.e. $|a|^2 = 1$. This will ensure that $|\psi(\vec{r} + \vec{\delta}, t)|^2 = |\psi(\vec{r}, t)|^2$. Eq. (1.25) has the solution $a = e^{\pm i\epsilon}$ if $B = \pm iA$.

<u>Proof</u>: The left hand side yields

$$\psi\left(\vec{r} + \vec{\delta}, t\right) = A\cos\left(\vec{k} \cdot \vec{r} - \omega t + \epsilon\right) + B\sin\left(\vec{k} \cdot \vec{r} - \omega t + \epsilon\right)$$
$$= A\left[\cos\left(\vec{k} \cdot \vec{r} - \omega t\right)\cos\epsilon - \sin\left(\vec{k} \cdot \vec{r} - \omega t\right)\sin\epsilon\right]$$
$$+ B\left[\sin\left(\vec{k} \cdot \vec{r} - \omega t\right)\cos\epsilon + \cos\left(\vec{k} \cdot \vec{r} - \omega t\right)\sin\epsilon\right] . \tag{1.26}$$

Upon plugging in $B = \pm iA$ we get

$$\psi\left(\vec{r} + \vec{\delta}, t\right) = A\left[\cos\left(\vec{k} \cdot \vec{r} - \omega t\right) \pm i\sin\left(\vec{k} \cdot \vec{r} - \omega t\right)\right]\cos\epsilon$$
$$\pm iA\left[\cos\left(\vec{k} \cdot \vec{r} - \omega t\right) \pm i\sin\left(\vec{k} \cdot \vec{r} - \omega t\right)\right]\sin\epsilon = \psi(\vec{r}, t)e^{\pm i\epsilon} . \tag{1.27}$$

☐ We have thus found an important property of quantum theory. We are forced to admit *complex valued* wave functions to accommodate experimental results. This fact is often phrased as "the phase of a free particle is not observable". Note the difference with electrodynamics where detectors exist that can detect the "amplitudes" $\vec{E}$ or $\vec{B}$ directly instead of just the intensities E^2 and B^2.

☐ We fix the choice $B = +iA$ and now have the general form of a plane wave permitted in quantum mechanics

$$\boxed{\psi(\vec{r}, t) = Ae^{i(\vec{k} \cdot \vec{r} - \omega t)}} . \tag{1.28}$$

☐ The (angular) frequency ω is yet undetermined. We expect it to be fixed by a *dispersion relation* $\omega = \omega(\vec{k})$ as for classical waves. We recall that experimental results indicate a relation between frequency and energy,

$$E = h\nu = \hbar\omega . \tag{1.29}$$

8

Using the usual relation $E = p^2/(2m)$ for free particles we can then postulate the dispersion relation

$$\boxed{\omega = \frac{\hbar}{2m} k^2}$$

(1.30)

for plane waves describing *free* particles of mass m. We will revisit this point in more detail below.

1.4 Wave Packets

The Fourier transformation is such an important tool in quantum mechanics that we review some basic properties before continuing.

1.4.1 Fourier Transformations

☐   Recall that for a suitable function $f : \mathbb{R}^n \to \mathbb{C}$ (or $\mathbb{R}$), $n \in \mathbb{N}$ we define the Fourier transformation as

$$\hat{f}(\vec{k}) = \frac{1}{\sqrt{2\pi}^n} \int_{\mathbb{R}^n} f(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} d^n r \,.$$

(1.31)

For most applications here $n = 3$ so we have used vector arrows for "positions" $\vec{x}$ and "wave vectors" $\vec{k}$. "Suitable" usually means that f has to be integrable (i.e. of type L^1) or square-integrable (L^2).[2] The Fourier transformed function $\hat{f}$ is again a function $\mathbb{R}^n \to \mathbb{C}$.

☐   Under certain conditions f can be recovered from $\hat{f}$ by the inverse Fourier transformation. Then

$$f(\vec{r}) = \frac{1}{\sqrt{2\pi}^n} \int_{\mathbb{R}^n} \hat{f}(\vec{k}) e^{i\vec{k}\cdot\vec{r}} d^n k \,.$$

(1.32)

☐   Fourier transformations can be extended to a certain class of *distributions* or *generalized functions*, most notably Dirac's δ-function. Recall that δ is defined in one dimension by

$$\int_I \delta(x) f(x) dx = f(0)$$

(1.33)

for any open interval I on the real line containing 0, and

$$\int_I \delta(x) f(x) dx = 0$$

(1.34)

for any other open interval. This has to hold for arbitrary *test functions* $f : \mathbb{R} \to \mathbb{R}$. Thus δ appears to be a function that vanishes everywhere except for the point 0 where it diverges. However, it can not be rigorously defined as a function that way.

☐   The Fourier transformed δ-function is a constant function, to be precise

$$\hat{\delta}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \delta(x) e^{-ikx} dx = \frac{1}{\sqrt{2\pi}} \,.$$

(1.35)

☐   More generally: the δ-function in 1 dimension shifted by a parameter y is the Fourier partner of (the spatial part) of a plane wave in y:

$$\delta(x - y) \xrightarrow{\text{Fourier}} \frac{1}{\sqrt{2\pi}} e^{-iky} \,.$$

(1.36)

---

[2]Mathematical background information is often mentioned but not emphasized in this course. Readers interested in more rigorous definitions and proofs are encouraged to read up in the mathematical literature, e.g. in the book of Fano.

<u>Proof</u>: We have

$$\hat{\delta}_y(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \delta(x-y)e^{-ikx} = \frac{1}{\sqrt{2\pi}}e^{-iky} \tag{1.37}$$

and conversely ... this will be a HW problem this year.

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{ikx}\hat{\delta}_y(k)dk = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ik(x-y)}dk = \delta(x-y) \tag{1.38}$$

For the last = sign one needs to check that the integral expression on its left hand side satisfies the defining properties of δ, i.e. it needs to be integrated over test functions to recover (1.33), (1.34). The proof goes as follows. We will only check property (1.33), as Eq. (1.34) can be quite readily seen. It is then also sufficient to show it for $I = \mathbb{R}$. Then using the antisymmetry of the sin-function twice the k-integral is

$$\frac{1}{2\pi} \int_{\mathbb{R}} \int_{\mathbb{R}} e^{ik(x-y)} f(x)\, dk dx = \frac{1}{2\pi} \int_{\mathbb{R}} \frac{1}{x-y} \sin k(x-y)\Big|_{k=-\infty}^{k=\infty} f(x)\, dx$$

$$= \frac{k}{\pi} \int_{\mathbb{R}} \lim_{k\to\infty} \frac{\sin k(x-y)}{k(x-y)} f(x)\, dx. \tag{1.39}$$

We realize that the sinc-function in the limit $k \to \infty$ becomes more and more narrow so that all its strength will lie at $x = y$. We can thus expand f around $u = 0$ and just replace it by $f(y)$. The integral then becomes independent of k and we easily substitute a new integration variable $u \equiv k(x-y)$ and using the well-known normalization of the sinc-function we get

$$\frac{k}{\pi} \int_{\mathbb{R}} \lim_{k\to\infty} \operatorname{sinc} k(x-y)\, f(y)dx = f(y)\frac{1}{\pi} \int_{\mathbb{R}} \operatorname{sinc} u\, du = f(y). \tag{1.40}$$

I.e. the reverse Fourier transform of the plane wave has indeed the properties of the δ-function.
□   The δ-function can be generalized to n dimensions in a straightforward way but we skip details here for brevity.
□   <u>Parseval's Theorem</u>. Let f, g, be functions $\mathbb{R}^n \to \mathbb{C}$ both integrable (L^1) and square-integrable (L^2), and let $\hat{f}$ and $\hat{g}$ be their Fourier transforms, respectively. Then

$$\boxed{\int_{\mathbb{R}^n} f(\vec{r})g^*(\vec{r})\, d^n r = \int_{\mathbb{R}^n} \hat{f}(\vec{k})\hat{g}^*(\vec{k})\, d^n k}. \tag{1.41}$$

<u>Proof</u>:

$$\int_{\mathbb{R}^n} \hat{f}(\vec{k})\hat{g}^*(\vec{k})\, d^n k = \frac{1}{(2\pi)^n} \int_{\mathbb{R}^n} \int_{\mathbb{R}^n} d^n r d^n r' \int_{\mathbb{R}^n} d^n k\, e^{-ik(x-x')} f(\vec{r})g^*(\vec{r})$$

$$= \int_{\mathbb{R}^n} \int_{\mathbb{R}^n} d^n r d^n r'\, \delta^n(\vec{r}-\vec{r'})f(\vec{r})g^*(\vec{r'}) = \int_{\mathbb{R}^n} d^n r\, f(\vec{r})g^*(\vec{r}) \tag{1.42}$$

□   <u>Corollary: Plancherel's Theorem</u>. From Parseval's Theorem it follows immediately that the Fourier transformation preserves L^2-norms, i.e.

$$\boxed{\int_{\mathbb{R}^n} |f(\vec{r})|^2\, d^n r = \int_{\mathbb{R}^n} |\hat{f}(\vec{k})|^2\, d^n k}. \tag{1.43}$$

10

☐ Transformation of derivatives. Let $f : \mathbb{R}^n \to \mathbb{C}$ be a differentiable function such that the Fourier transformation exists for f and for all of its partial derivatives $\partial f/\partial r_j$, $j = 1, \ldots, n$. Then we have

$$\widehat{\frac{\partial f}{\partial r_j}} = ik_j \hat{f} \tag{1.44}$$

i.e. derivatives are factors in Fourier space and vice versa.

Proof: By partial integration one can see that

$$\widehat{\frac{\partial f}{\partial r_j}} = \int_{\mathbb{R}^n} e^{-i\vec{k}\cdot r} \frac{\partial f}{\partial r_j} \, d^n r = \int_{\mathbb{R}^n} (ik_j) e^{-i\vec{k}\cdot r} f(\vec{r}) \, d^n r = ik_j \hat{f}(\vec{k}) \tag{1.45}$$

if boundary terms can be neglected, e.g. for square integrable functions.

1.4.2 Fourier Analysis of Wave Packets

☐ Plane waves with wave vector $\vec{k}$ describe free particles with sharply defined momentum $\vec{p} = \hbar \vec{k}$ which are unlocalized in space. The superposition principle allows us to build other solutions from plane waves which are localized in space. In general a free particle wave function could take the form

$$\boxed{\psi(\vec{r}, t) = \frac{1}{\sqrt{2\pi}^3} \int \phi(\vec{k}) e^{i(\vec{k}\cdot\vec{r} - \omega(\vec{k})t)} d^3 k} \tag{1.46}$$

if $\phi(\vec{k})$ is a suitable function (i.e. all the necessary integrals exist). This is generally called a *wave packet*.

☐ Obviously $\phi(\vec{k})$ is the Fourier transformation of the wave function $\psi(\vec{r}, 0)$ at $t = 0$, i.e.

$$\phi(\vec{k}) = \frac{1}{\sqrt{2\pi}^3} \int \psi(\vec{r}, 0) e^{-i\vec{k}\cdot\vec{r}} d^3 r \tag{1.47}$$

We sometimes switch variables from $\vec{k}$ to $\vec{p}$ and write $\phi(\vec{p})$. ϕ is thus usually referred to as the *wave function in momentum space*.

☐ For now let us analyze wave packets at a fixed point in time, say at $t = 0$. For simplicity let us start in 1 dimension. $\phi(k)$ describes the *distribution of modes* in the wave packet, i.e. the relative weights of plane waves of momentum k.

☐ Let us assume a typical case where $\phi(k)$ resembles some real-valued function which has a peak at $k = k_0$ and falls off monotonically on both sides with a characteristic width Δk around the peak. After introducing a new variable $u = k - k_0$ we can write the wave function as a product

$$\psi(x, t) = \frac{1}{\sqrt{2\pi}} e^{ik_0 x} H(x) \tag{1.48}$$

of a plane wave with the (most likely) momentum k_0 and a modulation function $H(x)$ ("hull"). For the latter we have

$$H(x) = \int \phi(u + k_0) e^{iux} \, du \,. \tag{1.49}$$

We can qualitatively analyze $H(x)$ in the following way.

- For small x (precisely: if $x \, \Delta k \ll \pi$) all the strength of the falling function $\phi(u+k_0)$ (centered around $u = 0$) is contained within one half period of the cos-function in e^{iux} and thus the integral defining H has its maximum value.

- For large x (precisely: if $x\,\Delta k \gg \pi$) many oscillations of e^{iux} lie within the width Δk of $\phi(u+k_0)$ and the integral for H is dominated by cancellations, hence the value of H is small.

Therefore $H(x)$ is a function centered around 0 that goes to zero on both sides with characteristic width $\Delta x \sim \pi/\Delta k$.

□ To summarize this qualitative argument, a wave packet of width Δk in momentum (or wave vector) space corresponds to a wave packet with width Δx in coordinate space, and the two widths are reciprocal to each other.

□ We just qualitatively confirmed Heisenberg's uncertainty principle, $\Delta x\,\Delta k \sim \mathcal{O}(1)$. This relation is a natural property of waves and not specific to quantum mechanics.

□ We can make this uncertainty relation mathematically precise. Let $f : \mathbb{R} \to \mathbb{C}$ be a differentiable function for which the Fourier transformation $\hat{f}$ exists. Furthermore let f have L^2-norm unity, i.e.

$$\int_{\mathbb{R}} |f|^2 dx = 1\,. \tag{1.50}$$

Let x_0 and k_0 be arbitrary points in coordinate space and wave vector space, respectively. We define the *variation* of f around x_0 and of $\hat{f}$ around k_0 as

$$(\Delta x)^2 = \int_{\mathbb{R}} (x - x_0)^2 |f(x)|^2\, dx\,, \tag{1.51}$$

$$(\Delta k)^2 = \int_{\mathbb{R}} (k - k_0)^2 |\hat{f}(k)|^2\, dk\,, \tag{1.52}$$

respectively.[3]

□ Heisenberg's Uncertainty Principle. In above situation the inequality

$$\boxed{\Delta x\,\Delta k \geq \frac{1}{2}} \tag{1.53}$$

holds.

    <u>Proof</u>: Here we will set $x_0 = 0$, $k_0 = 0$ for convenience but the following proof will go through with other choices as well. First we note that

$$(\Delta k)^2 = \int \left| k\hat{f}(k) \right|^2 dk = \int \left| \frac{d}{dx} f(x) \right|^2 dx \tag{1.54}$$

due to Plancherel's Theorem. Then we have due to Schwartz's Inequality[4]

$$(\Delta x)^2\, (\Delta k)^2 = \int |x f(x)|^2\, dx \int |f'(x)|^2\, dx$$

$$\geq \left| \int [x f(x)]^* f'(x)\, dx \right|^2 \geq \left| \Re \int [x f(x)]^* f'(x)\, dx \right|^2\,. \tag{1.55}$$

Since $\Re(f^* f') = (\Re f)(\Re f') + (\Im f)(\Im f') = d/dx\,|f|^2/2$ we find[5]

$$\Re \int x f^* f'\, dx = \frac{1}{2} \int x \frac{d}{dx} |f|^2 dx\,. \tag{1.56}$$

_____

[3] These are of course just the expectation values of $(x - x_0)^2$ and $(k - k_0)^2$.
[4] For suitable functions f, $g : \mathbb{R}^n \to \mathbb{C}$ Schwartz's Inequality states $|\int f^* g\, d^n r|^2 \leq (\int |f|^2\, d^n r)(\int |g|^2\, d^n r)$.
[5] We use the fraktur letters $\Re$ and $\Im$ to denote real and imaginary part of a complex number.

This leads us to the conclusion

$$(\Delta x)^2 \, (\Delta k)^2 \geq \left| \frac{1}{2} \int x \frac{d}{dx} |f|^2 dx \right|^2 \geq \frac{1}{4} \left| \int |f(x)|^2 dx \right|^2 = \frac{1}{4} \tag{1.57}$$

where the second to last step is by partial integration.

☐ This generalized version of the uncertainty principle contains the previous case of wave packets (where x_0 and k_0 are peaks of the distributions in coordinate and momentum space, resp., and Δx and Δk the widths around those) as a special case. We will rederive Heisenberg's Principle in a much more abstract setting later on.

☐ The Gauss function $e^{-\frac{x^2}{4\sigma^2}}$ is an example for which the uncertainty is minimal, i.e. $\Delta x \, \Delta k = 1/2$. In other words Gaussian wave packets have the smallest possible uncertainty. <u>Proof</u>: HW I.

☐ We can rewrite the uncertainty principle in terms of momentum instead of the wave number. It reads

$$\boxed{\Delta x \, \Delta p \geq \frac{\hbar}{2}}. \tag{1.58}$$

☐ The generalization of the Fourier analysis to more than one dimension is straightforward. In particular, for the uncertainty principle we have

$$\Delta x \, \Delta p_x \geq \frac{\hbar}{2} \quad , \quad \Delta y \, \Delta p_y \geq \frac{\hbar}{2} \quad , \quad \text{etc.} \tag{1.59}$$

1.4.3 Time Dependence of Wave Packets

☐ We now drop the requirement of a fixed time and look again at the general wave packet (1.46). Let us again assume that in momentum space $\phi(\vec{k})$ is centered around a wave vector $\vec{k}_0$ and let $\vec{k} = \vec{k}_0 + \vec{u}$. We can use a Taylor expansion for the frequency

$$\omega(\vec{k}) = \omega(\vec{k}_0) + \sum_{i=1}^{3} \frac{\partial \omega}{\partial k_i}\bigg|_{\vec{k}_0} u_i + \frac{1}{2} \sum_{i,j=1}^{3} \frac{\partial^2 \omega}{\partial k_i \partial k_j}\bigg|_{\vec{k}_0} u_i u_j + \dots . \tag{1.60}$$

For free particles we had postulated $\omega = \hbar k^2/(2m)$ and in that case the series terminates after the 2nd order.

☐ Using the Taylor expansion up to second order we can rewrite the wave packet (1.46) as

$$\psi(\vec{r}, t) = \frac{1}{(2\pi)^{3/2}} e^{i\vec{k}_0 \cdot \left(\vec{r} - \frac{\omega(\vec{k}_0)}{k_0} \hat{k}_0 t \right)} \int \phi(\vec{u}) e^{i\vec{u} \cdot \left(\vec{r} - \nabla_{\vec{k}} \omega(\vec{k}_0) t \right)} e^{i \frac{1}{2} \sum_{i,j} u_i u_j \nabla_{\vec{k}}^i \nabla_{\vec{k}}^j \omega(\vec{k}_0) t} du \tag{1.61}$$

We use the symbol $\hat{}$ sometimes to denote unit vectors. This form is quite intuitive. We see that the wave packet is a product of "carrier" wave with wave vector $\vec{k}_0$ and a *phase velocity*

$$v_{\text{ph}} = \frac{\omega(\vec{k}_0)}{k_0} \tag{1.62}$$

in the direction of $\vec{k}_0$, and an "envelope" given by the integral. The wave packet envelope is propagating with a *group velocity*

$$\vec{v}_{\text{gr}} = \nabla_{\vec{k}} \omega(\vec{k}_0) \,, \tag{1.63}$$

13

given by the first term in the integrand, with a correction given by the term with two gradients of ω.

□ If a wave packet is to describe localized particles we must identify the group velocity with the particle velocity $\vec{v}$, i.e.

$$\nabla_{\vec{k}}\omega = \vec{v} = \frac{\vec{p}}{m} = \frac{\hbar}{m}\vec{k}\,. \tag{1.64}$$

This is a differential equation for ω which has the solution $\omega = \hbar k^2/(2m)$ plus a constant of integration which we set equal to zero. Thus we find that the postulate of identifying the group velocity of the wave packet with the particle velocity results in the same dispersion relation that we found earlier.

□ Using this dispersion relation for free particles we can easily calculate the double gradients in the correction term and find as the final expression for a wave packet of free particles

$$\psi(\vec{r},t) = \frac{1}{(2\pi)^{3/2}}e^{i\vec{k}_0\cdot(\vec{r}-\vec{v}_{\rm ph}t)}\int \phi(\vec{u})e^{i\vec{u}\cdot(\vec{r}-\vec{v}_{\rm gr}t)}e^{i\frac{1}{2}\frac{\hbar}{m}u^2t}du\,. \tag{1.65}$$

We can summarize the connection between wave and particle properties as

$$\boxed{\begin{aligned} \vec{v}_{\rm ph} &= \frac{\omega(k_0)}{k_0}\hat{k}_0 = \frac{E}{p}\hat{p}\,, \\[2mm] \vec{v}_{\rm gr} &= \nabla_{\vec{k}}\omega(\vec{k}_0) = \frac{\vec{p}}{m}\,. \end{aligned}} \tag{1.66}$$
$$\tag{1.67}$$

where E and $\vec{p}$ are particle energy and momentum.

□ The correction term is ~ 1 as long as $u^2|t|\hbar/(2m) \ll 1$. That is for small times $|t| \ll 2m/[\hbar(\Delta k)^2]$ the wave packet propagates undisturbed. For large times the correction term is an oscillating phase and the wave packet starts to change shape. Further investigation will reveal that the wave packet is spreading for $t \to \pm\infty$. The example of spreading Gaussian wave packets will be treated as a HW problem.