

# Physics IV - Script of the Lecture

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October 21, 2006

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## 0 Introduction

**Webpage:** <http://www.exp-astro.phys.ethz.ch/PhysikIV>

**Topics:**

1. Failures of Classical Physics; particles and waves
2. The Schrödinger Equation
3. Position and momentum
4. Energy and Time
5. Particles in potentials
6. Harmonic oscillators
7. Observables and Operators
8. Angular Momentum
9. The Hydrogen Atom
10. Bosons and Fermions
11. Atoms

**Books:**

- Tipler & Mosca: Physik/Physics for Scientists and Engineers
- Phillips: Introduction to Quantum Mechanics  
This will be the book, the professor follows more or less.
- Cohen-Tannoudji, Diu, Laloë: Quantum Mechanics vol 1,2 (E/D/F)  
A classic book
- Messiah: Quantum Mechanics vol 1,2 (E/D)  
A classic book
- Schwabl: Quantenmechanik

# 1 The Limits of Classical Physics & Wave-Particle Duality

## 1.1 Classical Concepts

- We have particles
  - A particle is a discrete entity
  - It has a precise and well defined position and momentum
  - It's obeying Newton's Laws of Motion
  - In principle, the Physics of Particles is completely deterministic
- We also have the electromagnetic fields and waves
  - The electromagnetic fields pervade all space
  - They're governed by Maxwell's equations
  - We have wavelike disturbances which propagate through space

The fields and the particles interact via the Lorentz forces

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

and we've got the equivalent for gravity.

In 1900-1930 there were two revolutions in Physics: Relativity and Quantum Mechanics. The upshot of this was, that Classical Physics is only an approximation and it isn't valid on everyday scales (Quantum Mechanics) und speeds (Relativity).

## 1.2 Empirical Problems with classical Physics

### 1.2.1 Atomic structure & atomic spectra

Atoms consist of positive and neutral nuclei and negative electrons (that can be removed). In Classical Mechanics we assume, that the electrons do orbit like in the solar system

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$$F_g = G \frac{M_\odot m_p}{r^2} \quad F_e = \frac{1}{4\pi\epsilon_0} \frac{q^+ q^-}{r^2}$$

The orbits are ellipses (sun at a focus) with

$$r = \frac{p}{1 - e \cos \theta} \quad E = \frac{1}{2} m v^2 - G \frac{M m}{r} = -G \frac{M m}{2a}$$

$$P^2 = a^3 \frac{4\pi^2}{G(M + m)}$$

where  $P$  is the period. As we know, we can get any energy and any period.

Now, we've got two problems:

- Atoms gain or loose energy by absorbing or emitting light at particular frequencies
- The electrons are continuously accelerated, therefore they should loose energy through electromagnetic radiation

$$\frac{dE}{dt} = \frac{2}{3} \frac{q^2 a^2}{4\pi\epsilon_0 c^3} = \frac{q^2 a^2}{6\pi\epsilon_0 c^3}$$

This means, the orbits should decay and the electrons should spiral into the nucleus, which doesn't happen.

### 1.2.2 Photo-electric effect

If we have shining light on a metal surface, there are electrons ejected

☒

The incident power per unit area is

$$P = \varepsilon_0 \overline{E}^2 c$$

The Ejection of the electrons should not depend on  $\nu$ , but only on  $\overline{E}^2$ . What we see is different. For example, Mg requires  $\nu > 8.9 \cdot 10^{14}$ Hz.

### 1.2.3 Waves behaving as particles

Consider an electromagnetic radiation with very high frequency  $\nu$  like by X-rays and wavelength  $\lambda$

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The change of  $K \cdot (1 - \cos \theta)$  in  $\lambda$  and  $\nu$  of an X-ray radiation is a signature of particle-like behaviour.

### 1.2.4 Particles acting as waves

Interference (constructive or destructive adding of waves) is fundamentally a wave phenomena

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In about 1927, it was seen, that particles also show diffraction patterns. It was shown, that 54eV acted like a wave with  $\lambda = 0.17$ nm and 40keV like one with  $\lambda = 0.006$ nm. In 1999 it was even shown, that the same effect occurs with  $C_{60}$  molecules.

### 1.2.5 Summay - new ideas

- Consider waves as particles, with specific energy and momentum
- Consider particles as waves, with specific wavelength and frequency
- The enrgy loss/gain is restricted, so  $\Delta E$  is not continuous
- We've got a propagation as waves and an exchange of energy as particles

## 1.3 Reminder Interference & Diffraction

The Huygens-Fresnel Principle says: "Every point on the wavefront acts as the source of a secondary spherical wavefront (wavelet), with same frequence and speed. The amplitude of the field at any point is the superposition of their wavelets taking into account amplitude and phase".

### 1.3.1 Young's slits interference

Assume that the slits are very narrow and one-dimensional

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We have constructive interference if

$$d \sin \theta = n\lambda \quad n \in \mathbb{Z}$$

and destructive interference if

$$d \sin \theta = (n + 1/2)\lambda \quad n \in \mathbb{Z}$$

For a general  $\theta$ , the phase difference for two slits is

$$\delta = 2\pi \frac{d \sin \theta}{\lambda}$$

Place the screen far from the slits (i.e. at a distance  $L \gg d$ ). Then, the position on the screen is

$$y = L \tan \theta \sim L \sin \theta$$

This approximation is good for small  $\theta$  and the maxima and minima are equally spaced

$$\begin{aligned} y_{\max} &= \frac{n\lambda}{d} L & \theta_{\max} &= \frac{n\lambda}{d} \\ y_{\min} &= \left(n + \frac{1}{2}\right) \frac{\lambda}{d} L & \theta_{\min} &= \left(n + \frac{1}{2}\right) \frac{\lambda}{d} \end{aligned}$$

For the wave amplitude we get

$$\begin{aligned} E &= E_0 (\sin(\omega t) + \sin(\omega t + \delta)) \\ &= 2E_0 \cos\left(\frac{\delta}{2}\right) \sin\left(\omega t + \frac{\delta}{2}\right) \end{aligned}$$

The intensity is proportional to  $E^2 \propto \cos^2(\delta/2)$

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What about interference from multiple slits? We need to sum wavelets from all slits, e.g. using a “phasor diagram”

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The maximum always has the “vectors” aligned, i.e.  $\delta = n2\pi$ . We will have secondary maxima when

$$m\delta = (2n + 1)\pi$$

where  $m$  is the number of slits and  $m\delta$  the total angle rotated in the phasor diagram (in this case, the end of the phasor-sum is at the other side of the circle).

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If we have an infinite number of slits, the interference pattern looks like this

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### 1.3.2 Diffraction

Consider an interference from a finite sized aperture. Take for example light passing through an aperture of finite width and  $\infty$  length

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We can consider this composed of  $N$  finite elements for small  $\theta$ . The phase difference between adjacent apertures is

$$\delta = 2\pi \frac{\theta}{\lambda} \frac{a}{N}$$

The phasor diagram will become a circle as  $N$  goes to  $\infty$

☒

For the angle we get

$$N\delta = \frac{2\pi a\theta}{\lambda} \Rightarrow E_\theta = \frac{E_0\lambda}{\pi a\theta} \sin\left(\frac{\pi a\theta}{\lambda}\right)$$

Now we wet  $\phi = \frac{\pi a\theta}{\lambda}$  to get

$$E_\theta = \frac{E_0}{\phi} \sin\phi$$

The intensity we then can write as

$$I_0 \frac{\sin^2\phi}{\phi^2}$$

This leads us to the diffraction pattern

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For  $a \gg \lambda$ , we get that  $\theta_{\min} \rightarrow 0$  and for  $a \sim \lambda$ , that  $\theta_{\min} \rightarrow 1$ .

Now we can construct the actual pattern from 2 finite slits

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In two dimensions (e.g. by a rectangular aperture), we get something like

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and the intensity, we can write as

$$I = I_0 \frac{\sin^2\phi_a}{\phi_a^2} \frac{\sin^2\phi_b}{\phi_b^2} \quad \phi_a = \frac{\pi a\theta_a}{\lambda} \quad \phi_b = \frac{\pi a\theta_b}{\lambda}$$

### 1.3.3 Fourier Optics

Consider a general aperture

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Then we have

$$E(\theta, \phi) = \iint dx dy \cdot E_0 T(x, y) e^{-i \frac{2\pi}{\lambda} (\theta x + \phi y)}$$

where  $T(x, y)$  is the transmission function of the aperture. Set  $u = \lambda^{-1}x$ ,  $v = \lambda^{-1}y$  to get

$$E(\theta, \phi) = E_0 \lambda^2 \iint du dv \cdot T'(u, v) e^{-2\pi i (u\theta + v\phi)}$$

The diffraction/interference pattern is the Fourier Transform of the aperture scaled by  $\lambda$  and vice versa.

## 1.4 Thermal radiation and Planck's constant $h$

### 1.4.1 Introduction

All bodies emit electro magnetic radiation because of their temperature. We could write

$$\frac{dE(\lambda, \text{Temperature, material})}{dt} d\lambda = \frac{\text{rate of energy loss per unit area}}{\text{per unit time in the interval } \lambda \rightarrow \lambda + d\lambda}$$

Different materials absorb different fractions of incident electro magnetic radiation, described by the *absorption coefficient*  $a$  and the emission coefficient  $e$ . It was found empirically by Ritchie (1833), that the emission properties are the same as the absorption properties for all materials, i.e.

$$\frac{e}{a} = \text{const}$$

It was shown with an experiment like this



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where for the emissive power  $e$  and die absorptive power  $a$ , we have

$$e_\alpha a_\beta = e_\beta a_\alpha \Rightarrow \frac{e_\alpha}{a_\alpha} = \frac{e_\beta}{a_\beta}$$

We've got a maximum  $e$ , when  $a = 1$ , as by a body that absorbs all radiation falling on it (*black body*).

Consider a uniform temperature enclosure in equilibrium at a temperature  $T$

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It turns out, that the *energy density*  $u$  with  $[u] = \text{Jm}^{-3}$  depends only on the temperature  $T$ .

To proof this, we imagine a cavity like

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If we have  $u_A(T) > u_B(T)$ , then energy flows from  $A$  to  $B$ , when the shutter is opened.

$\Rightarrow$  When we close the shutter,  $T_A$  has gone down and  $T_B$  has gone, which is a violation of the second Law of Thermodynamics.

The radiation escaping from a small hole in a cavity is the same as from an ideal black body. But what is the form of  $u(T)$  and more specifically, what is the spectrum of thermal radiation  $u(\lambda, T)d\lambda$ , which is the energy density for the interval  $\lambda \rightarrow \lambda + d\lambda$  as  $f(T)$ ?

#### 1.4.2 Stefan-Boltzmann Law

We want to know, what's the total energy emitted by a Black Body

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where

$$\frac{dE}{dt} = \frac{Acu(T)}{4}$$

(see problem sheet 1). The answer is

$$\frac{dE}{dt} = \sigma AT^4$$

which Stefan got empirically and Boltzmann proves by theory.  $\sigma$  we call the *Stefan-Boltzmann constant*. Boltzmann did a Thermodynamic argument to prove it: Imagine a reflecting enclosure, containing some thermal radiation. It turns out, that the radiation pressure is equal to  $\frac{1}{3}u$ , where the 3 comes from the three dimensions.

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The work done is equal to

$$\Delta v(p(T) - p(T - dT)) = \Delta v dp = \frac{1}{3} \Delta v du$$

The efficiency is

$$\begin{aligned} \frac{1}{3} \frac{\Delta v dm}{\frac{4}{3} \Delta v u} &= \frac{dT}{T} \\ \Rightarrow \frac{dT}{T} &= \frac{1}{4} \frac{du}{u} \rightarrow u \propto T^4 \end{aligned}$$

The energy density  $u = aT^4$ .

The emission from the black body is

$$\frac{ac}{4} T^4 = \sigma T^4$$

per unit area.

### 1.4.3 Wien's Displacement Law

What can we say about the spectrum  $u(\lambda, T)d\lambda$ . Consider again a cavity undergoing a reversible expansion. In this case, the wavelengths  $\lambda$  are proportional to the cavity size.

$$\frac{\lambda_1}{\lambda_2} = \frac{\ell_1}{\ell_2} \quad \frac{d\lambda_1}{d\lambda_2} = \frac{\ell_1}{\ell_2}$$

Using exactly the same argument as before, we get

$$\frac{u(\lambda_1)}{T_1^4} d\lambda_1 = \frac{u(\lambda_2)}{T_2^4} d\lambda_2$$

For an adiabatic process, we have

$$d[Vu(\lambda) d\lambda] + p(\lambda) dV = 0 \quad p(\lambda) = \frac{1}{3} u(\lambda) d\lambda$$

where the first term is the change in energy and the second is the work.

$$\begin{aligned} d[3Vu(\lambda)] + p(\lambda) dV &= 0 \\ 3Vdp(\lambda) + 4p(\lambda) dV &= 0 \\ \rightarrow p(\lambda_1)V_1^{4/3} &= p(\lambda_2)V_2^{4/3} \\ \rightarrow u(\lambda_1)\ell_1^4 d\lambda_1 &= u(\lambda_2)\ell_2^4 d\lambda_2 \\ \rightarrow u(\lambda_1)\lambda_1^5 &= u(\lambda_2)\lambda_2^5 \end{aligned} \quad (1.1)$$

Back to Stefan's Law

$$\frac{p(\lambda_1)}{T_1^4} = \frac{p(\lambda_2)}{T_2^4}$$

Now we eliminate  $p(\lambda)$ , using equation 1.1 to get

$$T_1^4 V_1^{4/3} = T_2^4 V_2^{4/3} \Rightarrow T_1 \ell_1 = T_2 \ell_2 \Rightarrow T_1 \lambda_1 = T_2 \lambda_2$$

We have

$$\frac{u(\lambda_1)\lambda_1^5}{f(\lambda_1, T_1)} = \frac{u(\lambda_2)\lambda_2^5}{f(\lambda_2, T_2)}$$

$\Rightarrow$  The general result for  $u(\lambda, T)$  is

$$u(\lambda, T) = \frac{A}{\lambda^5} f(\lambda T)$$

We will also be interested in  $u(\nu) d\nu$  which is the energy per unit volume with  $\nu \rightarrow \nu + d\nu$  and

$$u(\nu, T) = B\nu^3 g\left(\frac{T}{\nu}\right) \quad \nu_{\max} \propto T \quad \lambda_{\max} \propto \frac{1}{T}$$

which is the general form of Wien's Displacement Law.

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### 1.4.4 Oscillators

Imagine a cavity surrounded by "oscillators", each with two degrees of freedom

$$\begin{aligned} x &= x_0 \sin \omega t \\ \dot{x} &= \omega x_0 \cos \omega t \\ \ddot{x} &= -\omega^2 x_0 \sin \omega t \end{aligned}$$

The energy of it will be constant as it oscillates and equal to

$$\varepsilon = \frac{1}{2} m\omega^2 x_0^2$$

The emission of electro magnetic waves from an oscillator is instantaneously equal to

$$\frac{dE}{dt} = \frac{q^2 a^2}{6\pi\epsilon_0 c^3}$$

(see Physics III). Therefore, the time average of this is

$$\overline{\frac{dE}{dt}} = \frac{1}{2} \frac{q^2 \omega^4 x_0^2}{6\pi\epsilon_0 c^3}$$

where we just put in  $a = \ddot{x}$  from above and

$$\frac{dE}{dt} = \frac{q^2 \omega^2}{6\pi\epsilon_0 c^3 m} \varepsilon$$

For the absorption we get the analogous result (without proof)

$$\frac{dE}{dt} = \frac{\pi q^2 u(\nu)}{4\pi\epsilon_0 3m}$$

where  $\omega = 2\pi\nu$ . In equilibrium, the absorption and the emission are equal and so we can then write

$$\frac{q^2 \omega^2 \varepsilon}{6\pi\epsilon_0 m c^3} = \frac{\pi q^2 u(\nu)}{4\pi\epsilon_0 3m} \Rightarrow u(\nu) = \frac{8\pi\nu^2}{c^3} \varepsilon$$

where  $\varepsilon$  is the energy of the oscillator. If we look at all oscillators on average, we get

$$u(\nu) = \frac{8\pi\nu^2}{c^3} \bar{\varepsilon}$$

where  $\bar{\varepsilon}$  is the average energy of all oscillators with frequency  $\nu$ . So we want to know what's the average energy as a function of  $T$ . We would expect it to be  $\bar{\varepsilon} = kT$  to get

$$u(\nu) = \frac{8\pi\nu^2}{c^3} kT$$

which is called the *Rayleigh Jeans formula*. It satisfies

$$u(\nu) = \nu^3 g\left(\frac{T}{\nu}\right)$$

but it can't be right, because  $u \rightarrow \infty$  as  $\nu \rightarrow \infty$ . This is known as the *ultraviolet catastrophe*. If we look, where  $\bar{\varepsilon} = kT$  comes from, we see that the analysis to get it assumes, that we have an infinite range of possible energies, weighted by the Boltzmann factor.

$$dn(\varepsilon) = \frac{N}{kt} e^{-\varepsilon/kT} d\varepsilon \Rightarrow \bar{\varepsilon} = \frac{\int_0^\infty \varepsilon \frac{N}{kT} e^{-\varepsilon/kT} d\varepsilon}{\int_0^\infty \frac{N}{kT} e^{-\varepsilon/kT} d\varepsilon} = kT$$

#### 1.4.5 Planck's hypothesis (1900)

Plank's idea was to ask, what happened, if we allowed only certain energies

$$\varepsilon_j = j\varepsilon_0 \quad j = \gamma = 0, 1, 2, \dots$$

Exactly as before, we had  $n_j = Ae^{-\varepsilon_j/kT}$ , but

$$\begin{aligned} N &= A + Ae^{-\varepsilon_0/kT} + Ae^{-2\varepsilon_0/kT} + Ae^{-3\varepsilon_0/kT} + \dots \\ &= \sum_{j=0}^{\infty} Ae^{-\varepsilon_j/kT} = \frac{A}{1 - e^{-\varepsilon_0/kT}} \\ E &= 0 + A\varepsilon_0 e^{-\varepsilon_0/kT} + A2\varepsilon_0 e^{-2\varepsilon_0/kT} + \dots \\ &= A \sum_{j=0}^{\infty} \varepsilon_j e^{-\varepsilon_j/kT} = \frac{A\varepsilon_0 e^{-\varepsilon_0/kT}}{(1 - e^{-\varepsilon_0/kT})^2} \end{aligned}$$

It follows

$$\bar{\varepsilon} = \frac{E}{N} = \frac{\varepsilon_0 e^{-\varepsilon_0/kT}}{(1 - e^{-\varepsilon_0/kT})} = \frac{\varepsilon_0}{(e^{\varepsilon_0/kT} - 1)}$$

and

$$u(\nu) d\nu = \frac{8\pi\nu^2}{3c^3} \frac{\varepsilon_0}{(e^{\varepsilon_0/kT} - 1)}$$

This works if  $u(\nu) = B\nu^3 g\left(\frac{T}{\nu}\right)$  if  $\varepsilon_0 \propto \nu$ , i.e.

$$\varepsilon_0 = h\nu \quad h = 6.625 \cdot 10^{-34} \text{ Js}$$

where  $h$  is *Planck's constant*. This then gives the final answer for black body radiation density

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

which is called *Planck's formula*. It reduces to

$$\frac{8\pi\nu^2}{3c^3} kT$$

for  $h\nu \ll kT$ . At the end we've got rid of the ultraviolet catastrophe by cutting out the continuity of the energy.

1905 Einstein quantised the radiation in a cavity and called this wave packets *photons* with

$$E = h\nu$$

This explained for example the photo-electric effect.

## 1.5 De Broglie waves & Planck's constant

The wavelike properties of matter were proposed by de Broglie in 1923 with

$$\lambda = \frac{h}{p}$$

where  $p$  is the momentum. In terms of energy we can rewrite this with

$$\varepsilon^2 = m_0^2 c^4 + p^2 c^2 \quad \Rightarrow \quad \lambda = \frac{hc}{\sqrt{\varepsilon - m_0 c^2} \sqrt{\varepsilon + m_0 c^2}}$$

In a highly relativistic case, i.e.  $\varepsilon \gg m_0 c^2$ , we can write

$$\lambda = \frac{hc}{\varepsilon}$$

which is identical to photons ( $\varepsilon = h\nu$ ). In the non-relativistic case, i.e. for  $\varepsilon = m_0 c^2 + E$ , where  $E = \frac{p^2}{2m_0}$  is the kinetic energy, we get

$$\lambda = \frac{h}{\sqrt{2m_0 E}}$$

For example, an energy of 1.5eV is a  $\lambda = 1\text{nm}$  and an energy of 15keV is a  $\lambda = 0.01\text{nm}$ .

## 1.6 Measurements & Planck's constant

This section is still largely classical and shouldn't be translated into Quantum Mechanical concepts.

We go through the "thought experiment" of *Heisenbergs microscope*

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We know, that the defraction from the aperture  $d$  is of the order  $\sim \frac{\lambda}{d}$ . The uncertainty  $\Delta x$  is going to be given by

$$\Delta x \sim \frac{\lambda}{d} z \sim \frac{\lambda}{\alpha}$$

The scattered photon from the electron must have entered the microscope and therefore, the photon has a momentum with

$$|p_x| < \frac{h}{\lambda} \sin \alpha < \frac{h\alpha}{\lambda}$$

For the electron, the uncertainty  $\Delta p$  in the momentum of the electron must be of order  $\sim \frac{h\alpha}{\lambda}$ . We get to the interesting fact

$$\Delta x \Delta p \geq h$$

The correct Quantum Mechanical formulation of this is

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

## 1.7 Wave paricle duality & quantum reality

Lets do a little thought experiment

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The electrons hit the detector with a statistical distribution, so we observe a diffraction pattern in the locations of the detected electrons. This implies wave properties through the slits. We could ask, whether we can tell which slit the electron passed through and indeed we can quite easily, but then, the diffraction pattern dissapears! For example, we could measure the momentum of the electron by the recoil of the screen. If you think about it, near to the center of the screen, we would expect

$$\Delta p_{\text{screen}} \sim p_e \frac{d}{D} \sim \frac{h}{\lambda_e} \frac{d}{D}$$

From the previous section we know that however we try to measure the momentum, we have an uncertainty in position that is

$$\Delta x \sim \frac{h}{\Delta p} \sim \frac{D\lambda_e}{d}$$

which is exactly the separation of the interference fringes. So, when we know which slit the electron passed through, we no longer observe wavelike properties. When there is no possibility of knowing this, we observe wavelike behavior. We could say: “The wave is covert”. “The act of measurement brings into existence a property”.

## 2 The Schrödinger Equation

### 2.1 Review of waves

#### 2.1.1 Sinusoidal waves

The simplest wave with definite *wavelength*  $\lambda$ , *wavenumber*  $k = \frac{2\pi}{\lambda}$  and definite *period*  $\tau$ , *angular frequency*  $\omega = \frac{2\pi}{\tau}$  and *frequency*  $\nu = \frac{1}{\tau}$  are sinusoidal waves as

$$\Psi(x, t) = A \cos(kx - \omega t)$$

The maxima move at speed  $\frac{\omega}{k}$ . The most general sinusoidal wave is

$$\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t) = Ae^{i(kx - \omega t)}$$

Note, that in Classical Physics we normally take the real part of the complex wave. In Quantum Mechanics you always consider the complex function.

#### 2.1.2 Superposition of waves

**Standing wave:** A standing wave we get from a superposition like

$$\begin{aligned} \Psi(x, t) &= A \cos(kx - \omega t) + A \cos(kx + \omega t) \\ &= 2A \cos(kx) \cos(\omega t) \end{aligned}$$

So we can separate the spacial and the temporal parts.

**Wave packets:** A wave packet is a superposition with similar  $k$

$$\Psi(x, t) = \int_{k-\Delta k}^{k+\Delta k} A \cos(k'x - \omega't) dk'$$

At  $t = 0$ , this simplifies to

$$\begin{aligned} \Psi(x, 0) &= \int_{k-\Delta k}^{k+\Delta k} A \cos(k'x) dk' \\ &= \cos(kx) S(x) \end{aligned}$$

where

$$S(x) = 2A\Delta k \frac{\sin(\Delta kx)}{\Delta kx}$$

☒

#### 2.1.3 Dispersion relations

Non-dispersive waves are governed by the classical wave-equation

$$\frac{\partial^2 \Psi}{\partial x^2} - \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} = 0$$

In three dimensions, this is

$$\nabla^2 \Psi - \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} = 0$$

The solutions of this equation are

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

where  $\omega^2 = c^2 k^2$  and where  $v_{\text{phase}} = \frac{\omega}{k} = c$  is the speed of a maximum in the wave. We call it *phase velocity*. Because of linearity, the superposition of solutions is also a solution.

Generally, waves are dispersive, that means they have a more complicated  $\omega, k$  relation as  $\frac{\omega}{k} \neq \text{const}$ . This is due to a more complicated wave equation. The phase velocity is equal to the speed of individual crests  $\frac{\omega}{k}$  and the group velocity is the speed of the point of the maximum constructive interference in a wave packet  $v_G = \frac{d\omega}{dk}$

☒

To see this, consider 2 sinusoidal waves with  $\omega_1, \omega_2, k_1, k_2$ . We have constructive interference, when the phases are the same

$$(k_1 x_{\max} - \omega_1 t) = (k_2 x_{\max} - \omega_2 t) \Rightarrow x_{\max} = \frac{\omega_1 - \omega_2}{k_1 - k_2} t = \frac{\Delta\omega}{\Delta k} t$$

e.g. for long wavelength water waves in deep water, we have

$$\omega = \sqrt{gk} \quad v_p = \frac{\omega}{k} = \sqrt{\frac{g}{k}} \quad v_G = \frac{d\omega}{dk} = \frac{1}{2} \sqrt{\frac{g}{k}} = \frac{1}{2} v_p$$

## 2.2 Particle wave equation

We want a wave equation for particles by looking at the dispersion relation (don't worry yet what the wave is). With de Broglie, we had

$$\lambda = \frac{h}{p} \quad k = \frac{2\pi}{\lambda} \Rightarrow p = \frac{h}{2\pi} k =: \hbar k$$

A particle with uncertain  $p$  is associated with a wave packet with a range of  $k$ .

$$\Delta p \sim \hbar \Delta k$$

The "length" of the wave packet

$$\Delta x \sim \frac{2\pi}{\Delta k}$$

Lets set the group velocity  $v_G$  equal to the velocity of the particle

$$\Rightarrow \frac{d\omega}{dk} = \frac{p}{m} = \frac{\hbar k}{m}$$

We integrate to find

$$\omega = \frac{\hbar k^2}{2m} + (\text{const})$$

One could ask, what wave equation this dispersion relation gives

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

or in three dimensions

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi$$

This is the *Schrödinger Equation* for a "free particle". Lets take a wave-function  $\Psi(x, t) = A e^{i(kx - \omega t)}$  and check

$$i\hbar(-i\omega) = -\frac{\hbar^2}{2m} - k^2 \Rightarrow \hbar\omega = \frac{\hbar^2 k^2}{2m}$$

*Note:*

- Such wave equations have always complex wave solutions.
- The Schrödinger-equation is linear, that means that any superposition of solutions is also a solution.

The most general solution then is

$$\Psi(x, t) = \int_{-\infty}^{\infty} A(k') e^{i(k'x - \omega t)} dk'$$

provided we set

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

A narrow range of  $k$  leads to a wave packet moving with speed

$$\frac{d\omega}{dk} = \frac{\hbar k}{m}$$

The uncertainty in  $p$  and in  $x$  ( $\Delta p$  and  $\Delta x$ ) are related by

$$\Delta p \sim \hbar \Delta k \quad \Delta x \sim \frac{2\pi}{\Delta k}$$

### 2.3 A Particle in a potential energy field $V(\mathbf{r})$

If a particle has a potential energy  $V(\mathbf{r})$  as well as a kinetic energy, we modify the Schrödinger-Equation like

$$i\hbar \frac{d\Psi}{dt} = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \Psi$$

We could try a solution of the form  $\Psi(x, t) = Ae^{i(kx - \omega t)}$  with  $V(x) = V_0$ , to get

$$E = \hbar\omega = \frac{\hbar^2 k^2}{2m} + V_0$$

### 2.4 The meaning of $\Psi(x, t)$

We'll first do a digression on probabilities and probability distributions.

Consider  $n$  discrete outcomes of an experiment  $x_n$ , each of which have a probability of occurring  $p_n$ . We know

$$\sum p_n = 1$$

We define the *expectation value* of  $x$  as the average value, if the experiment is repeated many times

$$\langle x \rangle = \sum_n x_n p_n$$

With the *standard deviation* in  $x$ ,  $\Delta x$ , we get the *variance*  $(\Delta x)^2$  and

$$(\Delta x)^2 = \sum_n (x_n - \langle x \rangle)^2 p_n = \langle x^2 \rangle - \langle x \rangle^2$$

Consider a continuous variable  $x$ , then  $p(x)dx$  is the probability of  $x$  between  $x$  and  $x + dx$ . Like above, we then have

$$\int_{\text{all } x} p(x) dx = 1$$

and furthermore

$$\langle x \rangle = \int_{\text{all } x} xp(x) dx \quad \langle x^2 \rangle = \int_{\text{all } x} x^2 p(x) dx$$

Now, recall classical waves in the two-slit experiment



☒

By superposition, we have  $\Psi = \Psi_A + \Psi_B$  and the intensity is proportional to  $\Psi^2$ . By a Quantum wave function, we also have  $\Psi = \Psi_A + \Psi_B$  and by analogy, we construct  $|\Psi|^2 = \Psi^* \Psi$ . But what does this quantity mean?

☒

*Born's interpretation* of  $\Psi(x, t)$  was the following

$$\Psi^*(\mathbf{r}, t) \Psi(\mathbf{r}, t) dV \quad \text{or} \quad \Psi^*(x, t) \Psi(x, t) dx$$

is the probability of finding a particle in the volume  $dV$  (or within the distance  $dx$ ) at the time  $t$ , when we do some suitable experiment.

As we go on, we can sometimes state some rules about how we have to work with our wave-functions. Here's the first one.

**Rule 1:** We must always normalize  $\Psi(\mathbb{R}, t)$ , such that

$$\int_{\text{all space}} \Psi^* \Psi dV = 1$$

□

If we have

$$\Psi(x, t) = \sum_j A_j e^{i(k_j x - \omega_j t)} \quad p_j = \hbar k_j$$

then we get a probability of measuring the momentum  $p_i$  which is proportional to  $|A_i|^2$ . We can generalize this with a continuous distribution

$$\Psi(x, t) = \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)} dk$$

which effectively is a Fourier Transform. We can also construct a Fourier transform pair as follows

$$\begin{aligned} \Psi(x, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \tilde{\Psi}(p, t) e^{\frac{ipx}{\hbar}} dp \\ \tilde{\Psi}(p, t) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-\frac{ipx}{\hbar}} dx \end{aligned}$$

We know

$$\int_{-\infty}^{\infty} \Psi^* \Psi dx = 1 \quad \Leftrightarrow \quad \int_{-\infty}^{\infty} \tilde{\Psi}^* \tilde{\Psi} dp = 1$$

where  $\Psi^* \Psi$  is the probability amplitude for  $x$  and  $\tilde{\Psi}^* \tilde{\Psi}$  the probability amplitude for  $p$ .

## 2.5 Expectation values and operators

Using the equations from above, we can write down in one dimension

$$\begin{aligned} \langle x \rangle &= \int x \Psi^* \Psi dx = \int \Psi^* x \Psi dx \\ \langle p \rangle &= \int p \tilde{\Psi}^* \tilde{\Psi} dp = \int \tilde{\Psi}^* p \tilde{\Psi} dp \end{aligned}$$

We can also calculate  $\langle p \rangle$  in the following way

$$\langle p \rangle = \int_{\text{all } x} \Psi^*(x, t) (-i\hbar) \frac{\partial}{\partial x} (\Psi(x, t)) dx$$

which we prove with

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int \tilde{\Psi}(p, t) e^{\frac{ipx}{\hbar}} dp$$

We get

$$\begin{aligned} -i\hbar \frac{\partial}{\partial x} \Psi(x, t) &= -i\hbar \frac{\partial}{\partial x} \left( \frac{1}{\sqrt{2\pi\hbar}} \int \tilde{\Psi}(p, t) e^{\frac{ipx}{\hbar}} dp \right) \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int p \tilde{\Psi}(p, t) e^{\frac{ipx}{\hbar}} dp \end{aligned}$$

and therefore it follows

$$\begin{aligned} \langle p \rangle &= \int \Psi^*(x, t) \left( -i\hbar \frac{\partial}{\partial x} \Psi(x, t) \right) dx \\ &= \int \Psi^*(x, t) \left( \frac{1}{\sqrt{2\pi\hbar}} \int p \tilde{\Psi}(p, t) e^{\frac{ipx}{\hbar}} dp \right) dx \\ &= \int \left( \frac{1}{\sqrt{2\pi\hbar}} \int \Psi^*(x, t) e^{\frac{ipx}{\hbar}} dx \right) p \tilde{\Psi}(p, t) dp \\ &= \int \tilde{\Psi}^* p \tilde{\Psi} dp \end{aligned}$$

So, we can write

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

Now we introduce the concept of operators. The operator for  $x$  is  $\hat{x} = x$  and the operator for  $p$  is  $\hat{p} = -i\hbar \frac{\partial}{\partial x}$ . It turns out, that any observable quantity can be represented by an operator. Furthermore, the operators for  $x^2$  and  $p^2$  are given by

$$\hat{x}^2 = x^2 = (\hat{x})^2 \quad \hat{p}^2 = -\hbar^2 \frac{\partial^2}{\partial x^2} = (\hat{p})^2$$

In three dimensions, we have

$$\hat{\mathbf{r}} = \mathbf{r} \quad \hat{\mathbf{p}} = -i\hbar \nabla$$

**Rule 2:** We can apply operators to get any expectation value

$$\langle \xi \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{\xi} \Psi dx$$

or with  $dV$  in three dimension. □

Lets look at the operator for the energy  $E$ . Classically, we can write it as

$$E = \frac{p^2}{2m} + V(\mathbf{r})$$

and we would expect the energy operator as

$$\hat{E} = \frac{\hat{p}^2}{2m} + V(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) =: \hat{H}$$

where  $\hat{H}$  is called the *Hamiltonian operator*. Now

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi \, dV$$

Now going back to Schrödingers-Equation, we see that

$$i\hbar \frac{\partial \Psi}{\partial t} = \left( -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right) \Psi = \hat{H} \Psi$$

### 3 Solutions to Schrödinger's Equation

#### 3.1 Separable solutions of definite energy

We had the Schrödinger-Equation for a particle in a potential

$$i\hbar \frac{\partial \Psi}{\partial t} = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \Psi$$

Now, we're looking for solutions

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})T(t)$$

We put it in

$$i\hbar \psi(\mathbf{r}) \frac{dT}{dt} = \left( -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi \right) T$$

and separate the variables

$$\frac{i\hbar}{T} \frac{dT}{dt} = \frac{1}{\psi} \left( -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi \right)$$

This equation is true for all  $t$  and for all  $\mathbf{r}$ , so the terms have to be equal to a constant  $K$ . It follows

$$\frac{dT}{dt} = -\frac{i}{\hbar} KT \Rightarrow T(t) = Ae^{-\frac{iKt}{\hbar}}$$

and on the other hand

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \psi = K\psi$$

So, we're looking for the eigenfunctions  $\psi_n$  of  $\hat{H}$  associated with the eigenvalues  $K_n$ , i.e.

$$\hat{H}\psi_n = K_n\psi_n$$

With  $\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})Ae^{-\frac{iK_n t}{\hbar}}$  we then get

$$\langle E \rangle = \int \Psi_n^* \hat{H} \Psi_n d^3r = \int \psi_n^* \hat{H} \psi_n d^3r = K_n$$

So,  $K_n$  is equal to the energy of the system and we can write

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

which is called the *time-independent Schrödinger equation*. We also get

$$\langle E^2 \rangle = \int \Psi^* \hat{H}^2 \Psi d^3r = E^2$$

and for the energy uncertainty, we get from before

$$\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = 0$$

So, if the wave function of a system is an eigenfunction of  $\hat{H}$ , the energy of the system is precisely determined and is equal to the eigenvalue  $E_n$  associated to the eigenfunction. If we make a measurement to determine the energy  $E$ ,  $\Psi$  becomes the eigenfunction associated with the actual value measured. This sort of strange idea is called the *collapse of the wave function* during the measurement.

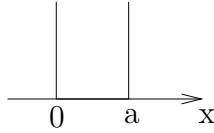
*Note:* The time part  $T$  is

$$T(t) = Ae^{-\frac{iE_n t}{\hbar}} \quad E_n = h\nu_n = \hbar\omega_n$$

### 3.2 Example: Particle in a box

Consider the potential

$$V(x) = \begin{cases} 0, & 0 < x < a \\ \infty, & \text{elsewhere} \end{cases}$$



We had the 1-dimensional Schrödinger-Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(\mathbf{r}) \right) \Psi$$

Look for separable solutions of it as

$$\Psi(x, t) = \psi(x) e^{-\frac{iE_n t}{\hbar}}$$

so we get

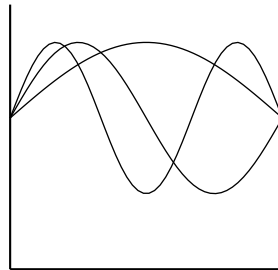
$$\left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right) \psi_n(x) = E_n \psi(x)$$

Inside the box,  $V = 0$  and with  $E_n = \frac{\hbar^2}{2m} k_n^2$  we get the equation

$$\frac{\partial^2 \psi}{\partial x^2} = -k_n^2 \psi$$

The boundary conditions are  $\psi(0) = 0$ ,  $\psi(a) = 0$ , so that  $\psi$  is continuous. Then the solutions are

$$\psi_n = A \sin k_n x \quad k_n = \frac{n\pi}{a}$$



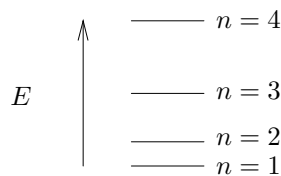
Now, for the  $n$ -th energy-state we get

$$E_n = \frac{n^2 \pi^2}{a^2} \frac{\hbar^2}{2m} \quad n = 1, 2, 3, \dots$$

and we can write

$$\Psi_n = A \sin\left(\frac{n\pi x}{a}\right) e^{-\frac{iE_n t}{\hbar}}$$

We can draw out these energy states



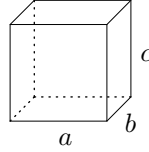
*Note:* The distance  $E_{n+1} - E_n$  goes up as we increase  $n$ , but

$$\frac{E_{n+1} - E_n}{E} \approx \frac{2}{n}$$

goes down as  $n$  and therefore the energy  $E$  gets bigger. The minimum  $E \neq 0$  we have for  $n = 1$ , so

$$E_1 = \frac{\hbar^2 \pi^2}{2m} \frac{1}{a^2}$$

For 3-dimensional potential wells



Its easy to show, that

$$\psi(x, y, z) = A \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$$

and of course then the energy of this system is

$$E(n_x, n_y, n_z) = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

We can see, that we have more complex energy-states, which lead to something like

☒

In dependency of  $a, b, c$  we can find equal energy-states  $E$  for different  $n_x, n_y, n_z$ . We call this *degeneracy*.

### 3.3 States of uncertain $E$

We represent more general states by a sum over the eigenstates

$$\Psi(\mathbf{r}, t) = \sum_{n=1}^{\infty} c_n \psi_n(\mathbf{r}) e^{-\frac{iE_n t}{\hbar}}$$

This is, because the eigenfunctions of  $\hat{H}$  form a complex orthonormal set of basis functions. That is

$$\int \psi_m^* \psi_n d^3r = \begin{cases} 1, & m = n \\ 0, & m \neq n \end{cases}$$

It is again easy to prove that

$$c_n = \int \Psi^*(\mathbf{r}, 0) \psi_n(\mathbf{r}) d^3r = \int \psi_n^*(\mathbf{r}) \Psi(\mathbf{r}, 0) d^3r$$

and then

$$\langle E \rangle = \sum_n |c_n|^2 E_n \quad \langle E^2 \rangle = \sum_n |c_n|^2 E_n^2$$

If the Quantum particle is represented by this general  $\Psi$ , that satisfies the conditions we've set, then the result of an experiment to measure  $E$  will be on  $E_n$  with probability  $|c_n|^2$ . Remember, that the eigenfunctions represent quantum states, with

- precisely defined energy  $E$
- observable properties that are time independent, like the position probability of the  $n$ -th quantum state

$$\Psi_n^* \Psi_n = \psi_n^* e^{\frac{iE_n t}{\hbar}} \psi_n e^{-\frac{iE_n t}{\hbar}} \neq f(t)$$

**Example 3.1:** We want to go through the example of a simple superposition

$$\Psi(\mathbf{r}, t) = \frac{1}{\sqrt{2}} \psi_1 e^{-\frac{iE_1 t}{\hbar}} + \frac{1}{\sqrt{2}} \psi_2 e^{-\frac{iE_2 t}{\hbar}}$$

Then we get

$$\langle E \rangle = \sum |c_n|^2 E_n = \frac{1}{2} (E_1 + E_2) \quad \langle E^2 \rangle = \frac{1}{2} (E_1^2 + E_2^2)$$

and therefore

$$\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} = \frac{1}{2} |E_1 - E_2|$$

Look at  $\Psi^* \Psi$  as function of  $t$

$$\Psi^* \Psi = \left( \frac{1}{2} \psi_1^* \psi_1 + \frac{1}{2} \psi_2^* \psi_2 + \frac{1}{2} \psi_1^* \psi_2 e^{\frac{i(E_1 - E_2)t}{\hbar}} + \frac{1}{2} \psi_2^* \psi_1 e^{-\frac{i(E_1 - E_2)t}{\hbar}} \right)$$

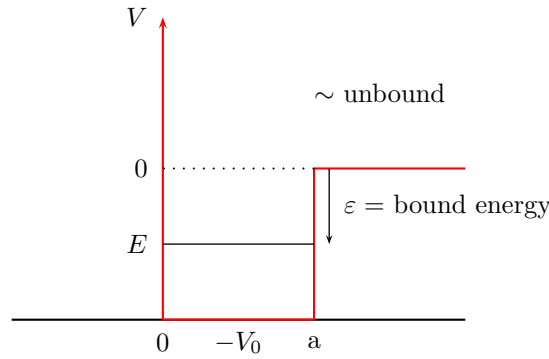
Therefore  $\Psi^* \Psi$  oscillates with frequency

$$\nu = \frac{E_1 - E_2}{h} \quad \text{or} \quad \omega = \frac{E_1 - E_2}{\hbar}$$

This of course is a non stationary state. The time scale for change is  $\delta t \propto \frac{1}{\Delta E}$ , where  $\delta t \Delta E \sim \hbar$ .  $\square$

### 3.4 Finite potential wells

Consider a  $V(x)$  as



Now we look for states of definite  $E$  solving

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi$$

where

$$V(x) := \begin{cases} \infty, & x < 0 \\ -V_0 & 0 < x < a \\ 0 & x > a \end{cases}$$

Set  $\psi(x)$  and  $\frac{\partial \psi}{\partial x}$  to be continuous at  $x = 0$ ,  $x = a$  (except  $\frac{\partial \psi}{\partial x}$  at  $x = 0$ ). Look first at the bound states with  $-V_0 < E < 0$ . For  $0 < x < a$ , we get

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2m}{\hbar^2} (E + V_0) \psi = -k_0^2 \psi$$

with  $k_0^2 = \frac{2m}{\hbar^2} (E + V_0)$ . This has the general solution

$$\psi_{\text{in}} = C \sin(k_0 x + \gamma)$$

where  $\gamma$  is an arbitrary phase. But  $\gamma = 0$  satisfies  $\psi = 0$  at  $x = 0$ , so

$$\psi_{\text{in}} = C \sin(k_0 x)$$

For  $x > a$ , we have

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{2mE}{\hbar^2} \psi = \alpha^2 \psi$$

with  $\alpha^2 = -\frac{2mE}{\hbar^2}$  and we get solutions

$$\psi_{\text{out}} = Ae^{-\alpha x} + A'e^{\alpha x}$$

We can set  $A' = 0$ , so that  $\psi$  doesn't blow up for  $x \rightarrow \infty$  (which wouldn't have any Physical meaning). Now stitch together the solutions at  $x = a$ . To get a continuous  $\psi(x)$ , we need

$$C \sin(k_0 a) = Ae^{-\alpha a}$$

and for the first derivative

$$k_0 C \cos(k_0 a) = -\alpha A e^{-\alpha a}$$

Dividing these, we get

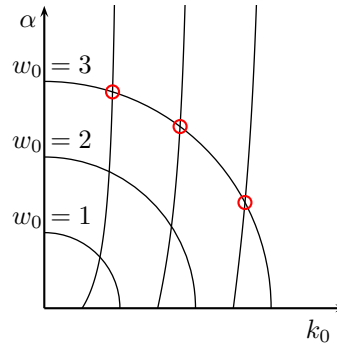
$$k_0 \cot(k_0 a) = -\alpha$$

About the energy, we know that

$$E = \frac{\hbar^2}{2m} k_0^2 - V_0 = -\frac{\hbar^2}{2m} \alpha^2 \quad V_0 = \frac{\hbar^2}{2m} w_0^2$$

where  $w_0$  is a measure of depth of the well. Now there are two things required

- 1)  $k_0^2 + \alpha^2 = w_0^2$
- 2)  $k_0 \cot(k_0 a) = -\alpha$



We have only one solution for  $k_0, \alpha$  for  $\frac{\pi}{2a} < \omega_0 < \frac{3\pi}{2a}$ , two for  $\frac{3\pi}{2a} < \omega_0 < \frac{5\pi}{2a}$  and so on.

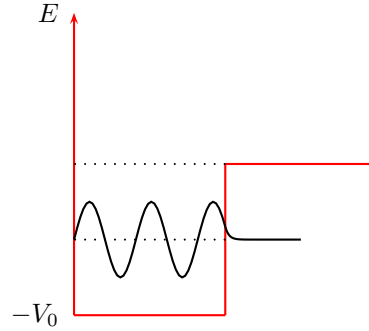


Note:

- The number of solutions depends on the well depth and it goes to  $\infty$  as  $-V_0 \rightarrow \infty$ .
- $\psi(x)$  for the bound states has an exponential tail extending into the classically forbidden region. That was essentially because

$$\psi_{\text{out}} \propto e^{-\alpha x} \quad \alpha^2 = \frac{2m\varepsilon}{\hbar^2}$$

We get a long tail, when  $\varepsilon$  is small and a small tail, when  $\varepsilon$  is very large.



Now, look at the unbound states  $E > 0$ . We write the energy for  $0 < x < a$  and  $x > a$

$$E = \frac{\hbar^2}{2m} k_0^2 - V_0 = \frac{\hbar^2}{2m} k^2$$

Then we write down the solutions

$$\begin{aligned} \psi_{\text{in}}(x) &= C \sin(k_0 x) \\ \psi_{\text{out}}(x) &= D \sin(kx - \delta) \end{aligned}$$

Now  $\psi(x)$  and  $\psi'(x)$  shall be continuous at  $x = a$ , so

$$\begin{aligned} C \sin(k_0 a) &= D \sin(ka + \delta) \\ k_0 C \cos(k_0 a) &= k D \cos(ka + \delta) \end{aligned}$$

After dividing them, we get

$$k_0 \cot(k_0 a) = k \cot(ka + \delta)$$

and as before

$$k_0^2 - k^2 = V_0 \frac{2m}{\hbar^2}$$

At the end, there's an infinite number of solutions for  $k$  and  $k_0$ , all with own  $\delta$ . This, if you like, makes sense.

Note: These are solutions for the stationary states. This does make sense for the unbound particle, because we can view stationary solutions as a standing wave due to a total reflection of particles at  $x = 0$ .

Introduce  $A_0 = -\frac{C}{2i}$ , then

$$\psi_{\text{in}} = A_0 e^{-ik_0 x} - A_0 e^{ik_0 x}$$

Now we can write

$$\Psi_{\text{in}} = A_0 e^{-ik_0 x - \frac{iEt}{\hbar}} - A_0 e^{ik_0 x - \frac{iEt}{\hbar}} = \psi_{\text{in}}(x) e^{-\frac{iEt}{\hbar}}$$

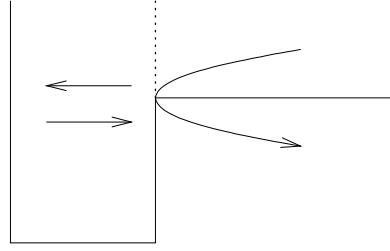
where the first term describes a travelling wave in negative  $x$ -direction and the second one a travelling wave in positive  $x$ -direction. For  $\Psi_{\text{out}}$ , introduce  $A = -\frac{D}{2i} e^{-i\delta}$ . Applying algebra, we get

$$\Psi_{\text{out}} = A e^{-ikx - \frac{iEt}{\hbar}} - A e^{2i\delta} e^{ikx - \frac{iEt}{\hbar}} = \psi_{\text{out}}(x) e^{-\frac{iEt}{\hbar}}$$

Here, the first term describes the incident and the second the reflected wave.

☒

*Note:* The reflected wave has a phase shift of  $2\delta$ . We'd like to know where this comes from



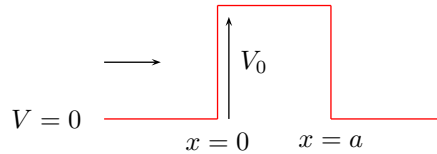
It is due to the time delay in traversing  $x = a$  to  $x = 0$  and back and therefore, we would expect  $\delta$  to be a function of the energy  $\delta(E)$ . In practice, the actual particles will have a range of  $E$  (like an uncertain  $E$ ) and then, there'll be a wave packet

$$\Psi_{\text{incident}} = \int_0^{\infty} c(E') e^{-i\left(\frac{E't}{\hbar} + \frac{p'x}{\hbar}\right)} dE' \quad p' = \sqrt{2mE'}$$

and the reflected wave will be

$$\Psi_{\text{reflected}} = \int_0^{\infty} c(E') e^{-i\left(\frac{E't}{\hbar} - \frac{p'x}{\hbar}\right)} e^{2i\delta(E')} dE'$$

### 3.5 Barrier penetration = “quantum tunnelling”



Classically, a particle will be reflected by the barrier. We use the same approach as before, so we solve the time-independent Schroedinger-Equation to get

$$\Psi(x, t) = \psi_E(x) e^{-\frac{iEt}{\hbar}} \quad -\frac{\hbar^2}{2m} \frac{d^2\psi_E}{dx^2} + V(x)\psi_E = E\psi_E$$

For  $x < 0$ , we have

$$\frac{d^2\psi_E}{dx^2} = -k^2\psi_E \quad E = \frac{\hbar^2 k^2}{2m}$$

because  $V(x) = 0$ . Therefore, we get the general solution

$$\Rightarrow \psi_E(x) = A_I e^{ikx} + A_R e^{-ikx}$$

where the first part is the incident component and the second part the reflected one.

For  $0 < x < a$ , we get two cases

a)  $E > V_0$ :

$$\frac{d^2\psi_E}{dx^2} = -k_0^2\psi_E \quad E = \frac{\hbar^2}{2m} k_0^2 + V_0$$

So we get the same solution as above, but with  $k_0$  instead of  $k$ .

b)  $E < V_0$ : This is classically forbidden, but here we get

$$\frac{d^2\psi_E}{dx^2} = \alpha^2\psi_E \quad E = -\frac{\alpha^2 \hbar^2}{2m} + V_0$$

which has as general solution

$$\rightarrow \psi_E(x) = B e^{-\alpha x} + B' e^{\alpha x}$$

For  $x > a$ , we get the same as for  $x < 0$ , means

$$\psi_E(x) = A_T e^{ikx}$$

where  $A_T$  can be complex to account for phasing.

Continuity at  $x = 0$  requires

$$A_I + A_R = B + B' \quad ikA_I - ikA_R = -\alpha B + \alpha B'$$

Continuity at  $x = a$  requires

$$B e^{-\alpha a} + B' e^{\alpha a} = A_T e^{ika} \quad -\alpha B e^{-\alpha a} + \alpha B' e^{\alpha a} = ik A_T e^{ika}$$

We set  $B' = 0$ , assuming that we have a “wide” barrier. So we get at  $x = 0$

$$2ikA_I \approx B(ik - \alpha)$$

and at  $x = a$

$$A_T e^{ika} \approx \frac{2\alpha}{(\alpha - ik)} B e^{-\alpha a}$$

Now eliminate  $B$  to get

$$\Rightarrow A_T e^{ika} \approx \frac{4ik}{(\alpha - ik)^2} \alpha e^{-\alpha a} A_I$$

The transmission probability then is

$$T = \left| \frac{A_T}{A_I} \right|^2 \approx \frac{16k^2 \alpha^2}{(\alpha^2 + k^2)^2} e^{-2\alpha a}$$

where

$$k^2 = \frac{2mE}{\hbar^2} \quad \alpha^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

Therefore, we can rewrite this as

$$T \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2\alpha a}$$

Remember, this is all right for  $e^{-2\alpha a} \ll 1$ . If we also have  $E \ll V_0$ , we can write

$$T \approx 16 \frac{E}{V_0} e^{-2\alpha a}$$

### Example 3.2: Fusion in stars

It turns out, that in the center of the sun, we have H and He gas at temperature  $T \sim 10^7$ K. The energy of a proton then is about

$$E_p = kT \sim 1\text{keV}$$

As protons approach with  $E \sim 1\text{keV}$ , the radius of closest approach is  $r \sim 10^{-12}$ m. To get to  $r \sim 10^{-15}$ m, which is necessary for fusion, we need an energy  $E \sim 1\text{MeV}$ . The Coulomb-Potential is

$$V(r) = \frac{q^2}{4\pi\epsilon_0 r} = \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r}$$

So, fusion should not occur classically at  $10^7$ K. We need to solve

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r} \right) \psi = E\psi \quad \mu = \frac{m_A m_B}{(m_A + m_B)}$$

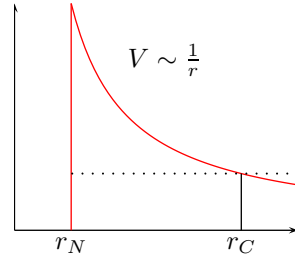
where  $\mu$  is the reduced mass.  $\psi(r)$  for a spherically symmetric wave function has the form

$$\psi(r) = \frac{u(r)}{r}$$

It turns out, that  $u(r)$  satisfies

$$\frac{-\hbar^2}{2m_r} \frac{d^2 u}{dr^2} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0} u = Eu$$

which is the same as in the one-dimensional case for  $x$ .



Now, the tunneling probability, we get by

$$T = \left| \exp \left( - \int_{r_N}^{r_C} \beta dr \right) \right|^2 \quad \beta(r) = \sqrt{\left( \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r} - E \right) \frac{2m}{\hbar^2}}$$

This leads us to

$$T \sim \exp \left( - \sqrt{E_G/E} \right) \quad E_G = \left( \frac{e^2}{4\pi\epsilon_0 \hbar c} \right)^2 2\pi^2 \mu c^2$$

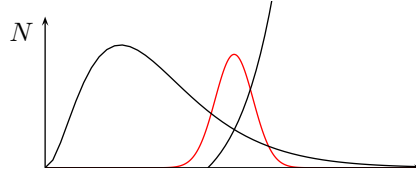
where we call  $E_G$  the *Gamow energy*. In numbers, this would be

$$T \sim e^{-22} \sim 3 \cdot 10^{-10}$$

by a temperature  $T \sim 10^7 \text{K}$  and therefore an  $E \sim 1 \text{keV}$ . The rate of fusion

$$\frac{dN}{dt} = e^{-\beta E^{-1/2}} e^{-\alpha E} n^2 \sigma V dE$$

where  $e^{-\beta E^{-1/2}}$  is the tunneling probability and  $e^{-\alpha E}$  is the Maxwellian distribution,  $n$  is the density



*Note:*

- 1) There is a sharp peak in energy of particles that can fuse  $e^{-\alpha E} e^{-\beta E^{-1/2}}$
- 2) The total rate is very strong temperature dependent

□

## 4 The Harmonic Oscillator

### 4.1 Classical case

We have the restoring force which is proportional to a displacement

$$F = -kx$$

and the potential

$$V(x) = \int_0^{\infty} kx' dx' = \frac{1}{2}kx^2$$

We can write down the differential equation

$$m \frac{d^2x}{dt^2} = -kx \leftrightarrow \ddot{x} = -\omega^2 x \quad \omega = \sqrt{\frac{k}{m}}$$

which has solutions

$$x = A \cos(\omega t + \alpha)$$

The total energy is

$$E_{\text{tot}} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 A^2$$

### 4.2 Quantum oscillator

#### 4.2.1 Stationary states

Lets write down the Hamiltonian in terms of the kinetic and the potential energy

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 \hat{x}^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

and Schrödinger's Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

Now look for stationary states, that is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n + \frac{1}{2}m\omega^2 x^2 \psi_n = E\psi_n$$

Change variables, i.e.  $E = \varepsilon\hbar\omega$ ,  $x = q\sqrt{\hbar/m\omega}$ , to get

$$\left(-\frac{d^2}{dq^2} + q^2\right) \psi(q) = 2\varepsilon\psi(q)$$

Remember

$$\begin{aligned} \left(q + \frac{d}{dq}\right) \left(q - \frac{d}{dq}\right) f(q) &= q^2 f - \frac{d^2}{dq^2} f - q \frac{df}{dq} + \frac{d}{dq} (qf) \\ &= \left(q^2 - \frac{d^2}{dq^2} + 1\right) f(q) \\ \left(q - \frac{d}{dq}\right) \left(q + \frac{d}{dq}\right) f(q) &= \left(q^2 - \frac{d^2}{dq^2} - 1\right) f(q) \end{aligned}$$

So we can write

$$\left(q + \frac{d}{dq}\right) \left(q - \frac{d}{dq}\right) \psi(q) = (2\varepsilon + 1) \psi(q)$$

and also

$$\left(q - \frac{d}{dq}\right) \left(q + \frac{d}{dq}\right) \psi(q) = (2\varepsilon - 1) \psi(q)$$

We can quickly find two solutions

a)  $\varepsilon = -1/2$ :

$$\left(q - \frac{d}{dq}\right) \Psi = 0 \quad \psi(q) = Ae^{\frac{1}{2}q^2}$$

which does not work, because the energy can't be negative.

b)  $\varepsilon = 1/2$ :

$$\left(q + \frac{d}{dq}\right) \psi = 0 \quad \psi(q) = Ae^{-\frac{1}{2}q^2}$$

This is the ground state of the oscillator, so if  $\varepsilon = 1/2$ , we have  $E_0 = \frac{1}{2}\hbar\omega$  and

$$\psi(q) = Ae^{-\frac{1}{2}q^2} \Rightarrow \psi_0(x) = Ae^{-\frac{x^2}{2a^2}} \quad a = \sqrt{\frac{\hbar}{m\omega}}$$

Now return to the eigenvalue equation

$$\begin{aligned} \left(q + \frac{d}{dq}\right) \left(q - \frac{d}{dq}\right) \psi_n(q) &= (2\varepsilon_n + 1) \psi_n(q) \\ \left(q - \frac{d}{dq}\right) \left(q + \frac{d}{dq}\right) \underbrace{\left(q - \frac{d}{dq}\right) \psi_n(q)}_{\psi_m} &= \underbrace{(2\varepsilon_n + 1)}_{2\varepsilon_m - 1} \underbrace{\left(q - \frac{d}{dq}\right) \psi_n(q)}_{\psi_m} \end{aligned}$$

but we had

$$\begin{aligned} \left(q - \frac{d}{dq}\right) \left(q + \frac{d}{dq}\right) \psi_m(q) &= (2\varepsilon - 1) \psi_m(q) \\ \Rightarrow 2\varepsilon_n + 1 &= 2\varepsilon_m - 1 \\ \Rightarrow \varepsilon_n &= \varepsilon_m - 1 \end{aligned}$$

So the operator

$$\left(q - \frac{d}{dq}\right)$$

is the operator to raise  $n$  by 1, means

$$\left(q - \frac{d}{dq}\right) \psi_n = \psi_{n+1}$$

Now apply the "raising operator" to  $\psi_0, \psi_1, \psi_2, \dots$ , so

$$\varepsilon_n = \varepsilon_0 + n\hbar\omega \Rightarrow E_n = \varepsilon_0 + n\hbar\omega$$

and

$$\begin{aligned} \psi_n(q) &= A_n \left(q - \frac{d}{dq}\right)^n e^{-\frac{1}{2}q^2} \\ \psi_n(x) &= A_n H_n \left(\frac{x}{a}\right) e^{-\frac{x^2}{2a^2}} \quad a = \sqrt{\frac{\hbar}{m\omega}} \end{aligned}$$

where  $H_n$  is a Hermite polynomial of  $\frac{x}{a}$ . We might write out some of the normalized functions

$$\begin{aligned} \psi_0(x) &= \left(\frac{1}{a\sqrt{\pi}}\right)^{\frac{1}{2}} e^{-\frac{x^2}{2a^2}} \\ \psi_1(x) &= \left(\frac{1}{2a\sqrt{\pi}}\right)^{\frac{1}{2}} 2\left(\frac{x}{a}\right) e^{-\frac{x^2}{2a^2}} \\ \psi_2(x) &= \left(\frac{1}{8a\sqrt{\pi}}\right)^{\frac{1}{2}} \left(2 - 4\left(\frac{x}{a}\right)^2\right) e^{-\frac{x^2}{2a^2}} \\ \psi_3(x) &= \left(\frac{1}{48a\sqrt{\pi}}\right)^{\frac{1}{2}} \left(12\left(\frac{x}{a}\right) - 8\left(\frac{x}{a}\right)^3\right) e^{-\frac{x^2}{2a^2}} \\ &\vdots \end{aligned}$$

Notes:

- 1)  $H_n$  has either odd or even powers of  $x$ , as  $n$  is odd or even, so

$$\psi_n(-x) = \psi_n(x)(-1)^n$$

- 2) The states (of definite  $E$ ) are time-independent (unlike the classical oscillator)

- 3)  $\psi^*\psi$  extends to  $x = \pm\infty$

- 4)  $\langle x \rangle = 0$  for all  $n$ , both sides are equally likely and

$$\langle x^2 \rangle = \left(n + \frac{1}{2}\right) a^2 \Rightarrow \Delta x = a\sqrt{n + \frac{1}{2}}$$

- 5)  $\langle p \rangle = 0$

$$\langle p^2 \rangle = \left(n + \frac{1}{2}\right) \frac{\hbar^2}{a^2} \Rightarrow \Delta p = \frac{\hbar}{a}\sqrt{n + \frac{1}{2}}$$

It follows

$$\Delta x \Delta p = \left(n + \frac{1}{2}\right) \hbar \geq \frac{\hbar}{2}$$

- 6) For the energies we get

$$\langle E_{\text{pot}} \rangle = \frac{1}{2}m\omega^2 \langle x^2 \rangle = \frac{1}{2}E_n \quad \langle E_{\text{kin}} \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{1}{2}E_n$$

To be sure, that  $\psi_0(x)$  is really the “ground state”, we look at the energy lowering operator  $\left(q + \frac{d}{dq}\right)$ , that is

$$\left(q + \frac{d}{dq}\right) \psi_n = \psi_{n-1} \quad \left(q + \frac{d}{dq}\right) \psi_0 = 0$$

where  $\psi_0$  has the term  $e^{-\frac{q^2}{2}}$  in it.

#### 4.2.2 Non-stationary states of uncertain energy

We write

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n t}{\hbar}}$$

The probability density in  $x$ , will oscillate in a complicated way

$$\begin{aligned} \Psi^* \Psi &= \sum_{n=1}^{\infty} \left(c_n^* \psi_n^* e^{i\frac{E_n t}{\hbar}}\right) \sum_{m=1}^{\infty} \left(c_m \psi_m e^{-i\frac{E_m t}{\hbar}}\right) \\ &= \sum_{n,m=1}^{\infty} c_n^* c_m \psi_n^* \psi_m e^{-i\frac{(E_m - E_n)t}{\hbar}} \end{aligned}$$

where

$$\omega_{m,n} = \frac{|E_m - E_n|}{\hbar}$$

is an integer multiple of  $\omega$ , but  $\langle x \rangle$  oscillates at only one frequency,  $\omega$

$$\begin{aligned} \langle x \rangle(t) &= \int_{-\infty}^{\infty} \Psi^* x \Psi dx \\ &= \sum_{m,n=1}^{\infty} c_m^* c_n e^{-i\frac{(E_n - E_m)t}{\hbar}} \int_{-\infty}^{\infty} \psi_n^* x \psi_m dx \end{aligned}$$

which is 0 unless  $|m - n| \leq 1$ . It is called the *quasi classical state*. In fact, we can find a set of  $c_n$ , so that  $\langle x \rangle$  and  $\langle p \rangle$  change with  $t$  as in the classical case

$$|c_n|^2 = \frac{\bar{n}^n}{n!} e^{-\bar{n}}$$

with  $\bar{n} \gg 1$ . This is called the *Poisson distribution*.

### 4.2.3 3-dimensional oscillator (degeneracy)

Now we solve the 3-dimensional  $\hat{H}$ , which is separable in  $x, y, z$

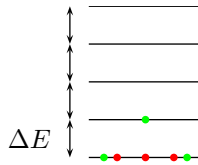
$$\begin{aligned}\hat{H}_x &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega_x^2 x^2 \\ \hat{H}_y &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{1}{2} m \omega_y^2 y^2 & \hat{H} &= \hat{H}_x + \hat{H}_y + \hat{H}_z \\ \hat{H}_z &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{1}{2} m \omega_z^2 z^2\end{aligned}$$

From this, we get directly

$$E_{n_x n_y n_z} = \left(n_x + \frac{1}{2}\right) \hbar \omega_x + \left(n_y + \frac{1}{2}\right) \hbar \omega_y + \left(n_z + \frac{1}{2}\right) \hbar \omega_z$$

or if  $\omega_x = \omega_y = \omega_z = \omega$

$$E_{n_x n_y n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right) \hbar \omega$$





## 5 Observables & Operators - Heisenberg Uncertainty Principle

### 5.1 Operators & eigenfunctions

We had the eigenvalue problem

$$\hat{H}\psi = E\psi$$

Having it resolved, we could decompose

$$\Psi(\mathbf{r}, t) = \sum_n c_n(t)\psi_n(\mathbf{r}) + \int c(E', t)\psi_{E'}(\mathbf{r}) dE'$$

where the sum is for the bound and the integral for the continuous case.  $|c_n(t)|^2$  is the probability, that we measure  $E_n$  and  $|c(E', t)|^2 dE'$  the probability, that we measure an energy  $E$  between  $E'$  and  $E' + dE'$ . We can now generalize this to any operator  $\hat{A}$  corresponding to an observable  $A$ , provided

- (1)  $\hat{A}$  must be a linear operator. So, if we have  $\hat{A}\psi_1 = \phi_1$  and  $\hat{A}\psi_2 = \phi_2$ , then

$$\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\phi_1 + c_2\phi_2$$

We need this because it allows the whole concept of superposition of states.

- (2)  $\hat{A}$  must be *Hermitian*, then

$$\int \Psi_1^* \hat{A} \Psi_2 d^3r = \int (\hat{A} \Psi_1)^* \Psi_2 d^3r$$

It guarantees that the eigenvalues of  $\hat{A}$  are real and that  $\langle A \rangle$  is real.

- (3) The eigenfunctions must form a complete basis set. So any  $\Psi$  can be represented as the sum or the integral of the eigenfunctions, one of which is “selected” when we make a measurement. We can rewrite generally

$$\Psi(\mathbf{r}, t) = \sum_n c_{a_n}(t)\psi_{a_n}(\mathbf{r}) + \int c(a', t)\psi_{a'}(\mathbf{r}) da'$$

where  $|c_{a_n}(t)|^2$  is the probability of measuring  $a = a_n$  and  $|c(a', t)|^2 da'$  is the probability of measuring  $a$  between  $a'$  and  $a' + da'$ .

### 5.2 Eigenfunctions for position and momentum

For the position, we have the equation

$$\hat{x}\psi_{x'}(x) = x'\psi_{x'}(x)$$

where  $\psi_{x'}(x)$  is the eigenfunction with eigenvalue  $x'$ . Because  $\hat{x} = x$ , we get

$$x\psi_{x'}(x) = x'\psi_{x'}(x)$$

This has the Dirac  $\delta$ -function as solution

$$\psi_{x'}(x) = \delta(x - x')$$

where by definition

$$\int_{-\infty}^{\infty} f(x)\delta(x - x') dx = f(x')$$

The eigenfunctions of position are continuous. Therefore, we can take our general decomposition equation in one dimension

$$\begin{aligned}\Psi(x, t) &= \int_{-\infty}^{\infty} c(x', t) \psi_{x'}(x) dx' \\ &= \int_{-\infty}^{\infty} c(x', t) \delta(x - x') dx' \\ &= c(x, t)\end{aligned}$$

where again  $|c(x, t)|^2 dx$  is the probability of finding a value between  $x$  and  $x + dx$ .

For the momentum, we get the eigenequation

$$\hat{p}\psi_{p'}(x) = p'\psi_{p'}(x)$$

which is equivalent to

$$-i\hbar \frac{\partial}{\partial x} \psi_{p'}(x) = p'\psi_{p'}(x)$$

It has the solutions

$$\psi_{p'}(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ip'x}{\hbar}}$$

where  $(2\pi\hbar)^{-1/2}$  is an arbitrary constant. We expect, that the function is either continuous in  $p'$  or discrete, so

$$\begin{aligned}\Psi(x, t) &= \int_{-\infty}^{\infty} c(p', t) \psi_{p'}(x) dp' \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} c(p', t) e^{\frac{ip'x}{\hbar}} dp'\end{aligned}$$

which is the Fourier integral from before with  $\tilde{\Psi}(p, t) = c(p, t)$ .

### 5.3 Compatible observables

There's an important idea: We can not necessarily specify a quantum state using different observables (c.f.  $x, p_x, y, p_y, z, p_z$  in classical mechanics), but we specify the position by a  $\Psi$  which is a superposition of momentum states and we specify the momentum by a  $\Psi$  which is a superposition of position states. The observables must be "compatible", but  $x, p$  are incompatible. To explore this, we introduce the *commutator of two operators*

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If  $[\hat{A}, \hat{B}] = 0$ , then  $A, B$  are compatible. If  $[\hat{A}, \hat{B}] \neq 0$ ,  $A, B$  are incompatible. We take  $\hat{x}, \hat{p}$

$$\begin{aligned}\hat{x}\hat{p}\Psi - \hat{p}\hat{x}\Psi &= x \left( -i\hbar \frac{\partial}{\partial x} \Psi \right) + i\hbar \frac{\partial}{\partial x} (x\Psi) \\ &= x(-i\hbar) \frac{\partial}{\partial x} \Psi + xi\hbar \frac{\partial}{\partial x} \Psi + i\hbar\Psi\end{aligned}$$

It follows

$$[\hat{x}, \hat{p}] = i\hbar \neq 0$$

It is easy to prove that there are no simultaneous eigenfunctions of  $\hat{x}$  and  $\hat{p}$ . If there were, we had

$$\hat{x}\psi_{x'p'}(x) = x'\psi_{x'p'}(x) \quad \hat{p}\psi_{x'p'}(x) = p'\psi_{x'p'}(x)$$

and therefore

$$[\hat{x}, \hat{p}] \psi_{x'p'}(x) = (x'p' - p'x') \psi_{x'p'}(x) = 0$$

It followed

$$i\hbar \psi_{x'p'}(x) = 0 \Rightarrow \psi_{x'p'}(x) = 0$$

Therefore, if we have a non-zero commutator, we have non identical eigenfunctions.

#### 5.4 Heisenberg uncertainty principle

We apply these ideas to get the uncertainties in  $x$  and  $p$ . The variance in  $x$  is

$$\begin{aligned} (\Delta x)^2 &= \langle x^2 \rangle - \langle x \rangle^2 = \int_{-\infty}^{\infty} \Psi^* (\widehat{\Delta x})^2 \Psi dx \\ (\Delta p)^2 &= \langle p^2 \rangle - \langle p \rangle^2 = \int_{-\infty}^{\infty} \Psi^* (\widehat{\Delta p})^2 \Psi dx \end{aligned}$$

Where  $\widehat{\Delta x} = \hat{x} - \langle x \rangle$  and  $\widehat{\Delta p} = \hat{p} - \langle p \rangle$ . So

$$[\widehat{\Delta x}, \widehat{\Delta p}] = (\hat{x} - \langle x \rangle)(\hat{p} - \langle p \rangle) - (\hat{p} - \langle p \rangle)(\hat{x} - \langle x \rangle) = [\hat{x}, \hat{p}] = i\hbar$$

To go on, we need to write down some general properties for Hermitian operators:

- (1) For the expectation value of  $A^2$ , where  $\hat{A}$  is Hermitian, we get

$$\langle A^2 \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{A}(\hat{A}\Psi) dx = \int_{-\infty}^{\infty} (\hat{A}\Psi)^*(\hat{A}\Psi) dx$$

- (2) With two Hermitian operators, we get  $\hat{A}$  and  $\hat{B}$

$$\begin{aligned} \int_{-\infty}^{\infty} \Psi^* \hat{A}\hat{B}\Psi dx &= \int_{-\infty}^{\infty} (\hat{A}\Psi)^* \hat{B}\Psi dx \\ &= \int_{-\infty}^{\infty} (\hat{B}\hat{A}\Psi)^* \Psi dx \\ &= \int_{-\infty}^{\infty} \Psi (\hat{B}\hat{A}\Psi)^* dx \\ &= \left( \int_{-\infty}^{\infty} \Psi^* \hat{B}\hat{A}\Psi dx \right)^* \end{aligned}$$

This implies, that the integral

$$\int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}]_+ \Psi dx = \int_{-\infty}^{\infty} \Psi^* (\hat{A}\hat{B} + \hat{B}\hat{A}) \Psi dx$$

is real and

$$\int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}] \Psi dx = \int_{-\infty}^{\infty} \Psi^* (\hat{A}\hat{B} - \hat{B}\hat{A}) \Psi dx$$

is purely imaginary.

- (3) *Schwarz' inequality*: Suppose  $\alpha(x)$ ,  $\beta(x)$  are complex functions of  $x$  with finite integrals

$$\int_{-\infty}^{\infty} \alpha^* \alpha \, dx, \quad \int_{-\infty}^{\infty} \beta^* \beta \, dx, \quad \int_{-\infty}^{\infty} \alpha^* \beta \, dx$$

Construct  $\phi(x) = \alpha + \lambda\beta$ ,  $\lambda \in \mathbb{C}$

$$\begin{aligned} \int_{-\infty}^{\infty} \phi^* \phi \, dx &= \int_{-\infty}^{\infty} \alpha^* \alpha \, dx + \lambda^* \lambda \int_{-\infty}^{\infty} \beta^* \beta \, dx \\ &\quad + \lambda^* \int_{-\infty}^{\infty} \beta^* \alpha \, dx + \lambda \int_{-\infty}^{\infty} \alpha^* \beta \, dx \geq 0 \end{aligned}$$

This is true for any  $\lambda$ , so true for

$$\lambda = \frac{- \int_{-\infty}^{\infty} \beta^* \alpha \, dx}{\int_{-\infty}^{\infty} \beta^* \beta \, dx}$$

It follows

$$\lambda^* \int_{-\infty}^{\infty} \beta^* \alpha \, dx = -\lambda^* \lambda \int_{-\infty}^{\infty} \beta^* \beta \, dx$$

and therefore

$$\begin{aligned} \int \phi^* \phi \, dx &= \int_{-\infty}^{\infty} \alpha^* \alpha \, dx - \frac{\int_{-\infty}^{\infty} \alpha^* \beta \, dx \int_{-\infty}^{\infty} \beta^* \alpha \, dx}{\int_{-\infty}^{\infty} \beta^* \beta \, dx} \\ &\geq 0 \end{aligned}$$

That is

$$\int \alpha^* \alpha \, dx \int \beta^* \beta \, dx \geq \int \alpha^* \beta \, dx \int \beta^* \alpha \, dx = \left| \int_{-\infty}^{\infty} \alpha^* \beta \, dx \right|^2$$

Now, set  $\alpha = \hat{A}\Psi$  and  $\beta = \hat{B}\Psi$  to get

$$\begin{aligned} \langle A^2 \rangle \langle B^2 \rangle &\stackrel{(1,3)}{\geq} \left| \int_{-\infty}^{\infty} (\hat{A}\Psi)^* (\hat{B}\Psi) \, dx \right|^2 \\ &= \left| \int_{-\infty}^{\infty} \Psi^* \hat{A} \hat{B} \Psi \, dx \right|^2 \\ &= \left| \int_{-\infty}^{\infty} \Psi^* \frac{1}{2} \left( [\hat{A}, \hat{B}]_+ + [\hat{A}, \hat{B}] \right) \Psi \, dx \right|^2 \\ &\stackrel{(2)}{=} \left| \frac{1}{2} \int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}]_+ \Psi \, dx \right|^2 + \left| \frac{1}{2} \int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}] \Psi \, dx \right|^2 \\ &= \frac{1}{4} \left| \int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}]_+ \Psi \, dx \right|^2 + \frac{1}{4} \left| \int_{-\infty}^{\infty} \Psi^* [\hat{A}, \hat{B}] \Psi \, dx \right|^2 \end{aligned}$$

It follows

$$\langle \Delta x \rangle^2 \langle \Delta p \rangle^2 \geq \frac{1}{4} \hbar^2 + \left| \int \Psi^* [\hat{x}, \hat{p}]_+ \Psi dx \right|^2$$

which gives us the Heisenberg uncertainty inequality

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

If we want equality, we also need

$$\int_{-\infty}^{\infty} \psi * [\hat{x}, \hat{p}]_+ \psi dx = 0$$

*Note:* In three dimensions, we can “mix” the position and momentum observables to specify a state, like  $x, y$  and  $p_z$

$$[\hat{x}, \hat{y}] = 0 \quad [\hat{x}, \hat{p}_z] = 0 \quad [\hat{y}, \hat{p}_z] = 0$$

Then we could write any wave function as superposition of functions

$$\psi_{x'y'p'_z} = \frac{1}{\sqrt{2\pi\hbar}} \delta(x - x') \delta(y - y') e^{-\frac{ip'_z z}{\hbar}}$$

which are the eigenfunctions of  $\hat{x}$ , also  $\hat{y}$ , also  $\hat{p}_z$ .

## 5.5 Compatibility with $\hat{H}$

Consider the expectation value for an observable  $A$  for a particle with wave function  $\Psi(\mathbf{r}, t)$

$$\langle A(t) \rangle = \int_{\mathbb{R}^3} \Psi(\mathbf{r}, t)^* \hat{A} \Psi(\mathbf{r}, t) d^3 \mathbf{r}$$

Using Schrödinger's Equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t)$$

we get

$$\begin{aligned} \frac{d}{dt} \langle A(t) \rangle &= \int_{\mathbb{R}^3} \frac{\partial \Psi^*}{\partial t} \hat{A} \Psi d^3 \mathbf{r} + \int_{\mathbb{R}^3} \Psi^* \hat{A} \frac{\partial \Psi}{\partial t} d^3 \mathbf{r} \\ &= -\frac{1}{i\hbar} \int_{\mathbb{R}^3} (\hat{H} \Psi)^* \hat{A} \Psi d^3 \mathbf{r} + \frac{1}{i\hbar} \int_{\mathbb{R}^3} \Psi^* \hat{A} \hat{H} \Psi d^3 \mathbf{r} \\ &= \frac{1}{i\hbar} \int_{\mathbb{R}^3} \Psi^* (\hat{A} \hat{H} - \hat{H} \hat{A}) \Psi d^3 \mathbf{r} \\ &= \frac{1}{i\hbar} \int_{\mathbb{R}^3} \Psi^* [\hat{A}, \hat{H}] \Psi d^3 \mathbf{r} \end{aligned}$$

where by the first step we assume that  $\hat{A} \neq f(t)$ . If  $\hat{A}$  is compatible with  $\hat{H}$ , i.e.  $[\hat{A}, \hat{H}] = 0$ , then

$$\frac{d \langle A \rangle}{dt} = 0$$

that means,  $A$  is a constant of motion.

## 5.6 Orbital angular momentum

Classically, the angular momentum is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

In Quantum Mechanics, we write

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla$$

or

$$\begin{aligned}\hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)\end{aligned}$$

It is easy to show by expanding, that for  $i = x, y, z$

$$\begin{aligned}[\hat{L}_x, \hat{L}_y] &= \hat{L}_z [\hat{z}, \hat{p}_z] \\ [\hat{L}_y, \hat{L}_z] &= \hat{L}_x [\hat{x}, \hat{p}_x] \\ [\hat{L}_z, \hat{L}_x] &= \hat{L}_y \underbrace{[\hat{y}, \hat{p}_y]}_{=i\hbar \neq 0}\end{aligned}$$

but that

$$[\hat{\mathbf{L}}^2, \hat{L}_x] = [\hat{\mathbf{L}}^2, \hat{L}_y] = [\hat{\mathbf{L}}^2, \hat{L}_z] = 0$$

We can also verify, that

$$[\hat{L}_i, \nabla^2] = 0 \quad [\hat{L}_i, V(r)] = 0$$

It follows

$$[\hat{L}_i, \hat{H}] = 0$$

for all  $\hat{H}$  associated with a “central potential  $V(r)$ ”

$$\Rightarrow [\hat{\mathbf{L}}^2, \hat{H}] = 0$$

As expected,  $L$  is conserved in a central potential. The most surprising thing is that we can define (or measure) the total  $L^2$ , plus only one component of it. Conventionally, we take  $L_z$ .

## 5.7 Angular momentum eigenfunctions

We first explore a Cartesian function

$$\psi_{(0,0)} = R(r)$$

so a spherically symmetric function. We go on with

$$\psi_{(1,0)} = R(r) \frac{z}{r} \quad \psi_{(1,+1)} = R(r) \frac{x+iy}{r} \quad \psi_{(1,-1)} = R(r) \frac{x-iy}{r}$$

Now we want to know what happens, if we apply  $\hat{L}_x$ ,  $\hat{L}_y$ ,  $\hat{L}_z$  and  $\hat{\mathbf{L}}^2$

- $\psi_{(0,0)}$ : We get

$$\begin{aligned}\hat{L}_x \psi_{(0,0)} &= -i\hbar \left( y \frac{\partial R}{\partial r} \frac{\partial r}{\partial z} - z \frac{\partial R}{\partial r} \frac{\partial r}{\partial y} \right) \\ &= -i\hbar \frac{\partial R}{\partial r} \left( y \frac{z}{r} - z \frac{y}{r} \right) = 0\end{aligned}$$

Any spherically symmetric  $\psi$  has  $\mathbf{L}^2 = L_x = L_y = L_z = 0$  and therefore

$$\begin{aligned}\hat{L}_x \psi_{(0,0)} &= 0\psi_{(0,0)} & \hat{L}_y \psi_{(0,0)} &= 0\psi_{(0,0)} & \hat{L}_z \psi_{(0,0)} &= 0\psi_{(0,0)} \\ \hat{\mathbf{L}}^2 \psi_{(0,0)} &= 0\end{aligned}$$

- $\psi_{(1,0)}$ : First we write down, that

$$\hat{\mathbf{L}} \left( \frac{R(r)}{r} z \right) = z \hat{\mathbf{L}} \left( \frac{R(r)}{r} \right) + \frac{R(r)}{r} \hat{\mathbf{L}} z = \frac{R(r)}{r} \hat{\mathbf{L}} z$$

Furthermore, we get

$$\begin{aligned} \hat{L}_x \psi_{(1,0)} &= \frac{R(r)}{r} \hat{L}_x z = -i\hbar \frac{R(r)}{r} y \\ \hat{L}_y \psi_{(1,0)} &= i\hbar \frac{R(r)}{r} x \\ \hat{L}_z \psi_{(1,0)} &= 0 \end{aligned}$$

$\psi_{(1,0)}$  is not an eigenfunction of  $\hat{L}_x$  or  $\hat{L}_y$ , but is of  $\hat{L}_z$ , with eigenvalue 0. Going on, we get

$$\hat{L}_x^2 \psi_{(1,0)} = \hbar^2 \frac{R(r)}{r} z = \hbar^2 \psi_{(1,0)} = \hat{L}_y^2 \psi_{(1,0)}$$

and therefore

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = 2\hbar^2 \psi_{(1,0)}$$

so  $\psi_{(1,0)}$  is also an eigenfunction of  $\hat{\mathbf{L}}^2$  with eigenvalue  $2\hbar^2$ .

- $\psi_{(1,1)}$ :

$$\psi_{(1,1)} = R(r) \frac{x + iy}{r}$$

$\psi_{(1,1)}$  is an eigenfunction of  $\hat{\mathbf{L}}^2$  with

$$\hat{\mathbf{L}}^2 \psi_{(1,1)} = 2\hbar^2 \psi_{(1,1)}$$

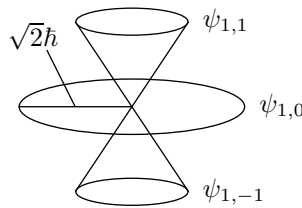
and an eigenfunction of  $\hat{L}_z$  with

$$\hat{L}_z \psi_{(1,1)} = \hbar \psi_{(1,1)}$$

- $\psi_{(1,-1)}$ :

$$\hat{L}_z \psi_{(1,-1)} = -\hbar \psi_{(1,-1)} \quad \hat{\mathbf{L}}^2 \psi_{(1,-1)} = 2\hbar^2 \psi_{(1,-1)}$$

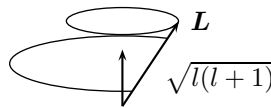
This can be illustrated in the following way



All this is much easier in spherical coordinates  $(r, \theta, \phi)$ , then  $\hat{L}_z$  and  $\hat{\mathbf{L}}^2$  operate on spherical harmonic functions, where

$$\begin{aligned} \hat{\mathbf{L}}^2 (Y_{\ell m}(\theta, \phi)) &= \ell(\ell + 1) \hbar^2 Y_{\ell m}(\theta, \phi) \\ \hat{L}_z (Y_{\ell m}(\theta, \phi)) &= m\hbar Y_{\ell m}(\theta, \phi) \end{aligned}$$

with  $m = -\ell, -\ell + 1, \dots, 0, \dots, \ell$ .



Note that  $\psi_{0,0} \propto Y_{00}$ ,  $\psi_{1,-1} \propto Y_{1,-1}$ , ... and that  $Y_{\ell m}$  are orthonormal

$$\int_0^{2\pi} \int_0^\pi Y_{\ell m}^* Y_{\ell' m'} \sin \theta \, d\theta \, d\phi = \delta_{mm'} \delta_{\ell\ell'}$$

So we have the two important things

- (1)  $L^2$  and  $L_z$  define orbital angular momentum quantum states
- (2) The orbital angular momentum is quantised in units of  $\hbar$

$$L = \sqrt{\ell(\ell+1)} \hbar \quad L_z = 0, \pm 1\hbar, \pm 2\hbar, \dots, \pm \ell\hbar$$

## 5.8 Stern-Gerlach experiment

The angular momentum of charged particles lets us expect a magnetic moment  $\boldsymbol{\mu}$ . e.g. for the electron

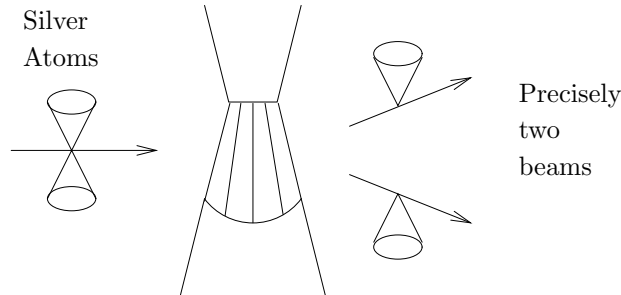
$$\mu_z^{\text{orbital}} = \frac{-e}{2m_e} L_z = -\frac{e}{2m_e} m_\ell \hbar$$

and for the spin

$$\mu_z^{\text{spin}} = \frac{-2e}{2m_e} S_z = -\frac{e}{m_e} m_s \hbar$$

Recall that  $\boldsymbol{\mu}$  in an inhomogeneous  $\mathbf{B}$  field suffers a force

$$F_z = \mu_z \frac{\partial B}{\partial z}$$



The result is, that we get exactly two beams, that is  $L_z$  is quantised by  $\pm \frac{1}{2} \hbar$ .

## 5.9 Spin

We have an angular momentum also from the spin of particles, which is not really meaningful as classical spinning object. There we have eigenvalues

$$S = \sqrt{s(s+1)} \hbar$$

and  $m_s = -s, -s+1, \dots, s-1, s$ , but  $s$  can now be a half-integer. The electron for example has  $s = \frac{1}{2}$  and therefore  $m_s = \pm \frac{1}{2}$  or the  $W$ -Boson has  $s = 1$  and therefore  $m_s = -1, 0, 1$ .



## 6 The Hydrogen Atom

### 6.1 Motion in “central potentials”

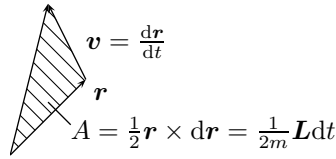
The hydrogen atom is the simplest one, because it is a proton  $p^+$  and an orbiting electron  $e^-$ . We say  $e^-$  orbits, because  $m_p \gg m_e$ . There we have a central potential

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{-e^2}{r}$$

which is as known similar to the potential of planetary motions. The central force acts radially and therefore, the angular momentum  $\mathbf{L}$  is conserved

$$\mathbf{F} = -\frac{dV}{dr} \hat{\mathbf{r}} \quad \mathbf{L} = m\mathbf{r} \times \mathbf{v} = m\mathbf{r} \times \frac{d\mathbf{r}}{dt} \quad \mathbf{N} = \mathbf{r} \times \mathbf{F} = 0$$

where  $\mathbf{N}$  is the torque.



We can split the momentum into a radial and a tangential part

$$p_r = m \frac{dr}{dt} \quad p_t = \frac{L}{r}$$

The kinetic energy then is given by

$$\frac{p^2}{2m} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2}$$

and therefore the total energy by

$$E = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r) = \frac{p_r^2}{2m} + V_e \quad V_e := \frac{L^2}{2mr^2} + V(r)$$

where we call  $V_e$  the *effective potential* with *effective force*

$$F_e = -\frac{dV_e}{dr} = \frac{L^2}{mr^3} - \frac{dV}{dr}$$

### 6.2 Solutions of Schrödingers equation in a central potential

For a wave function, describing a quantum state with sharply defined energy  $E$ , we write

$$\Psi(r, \theta, \phi, t) = \psi(r, \theta, \phi) e^{-\frac{iEt}{\hbar}}$$

where  $\psi(r, \theta, \phi)$  is an energy eigenfunction satisfying the eigenvalue equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi = E\psi \quad (6.1)$$

If we also assume, that the quantum state has as well definite angular momentum properties, we can write

$$\psi(r, \theta, \phi) = R(r) Y_{\ell, m_\ell}(\theta, \phi) \quad (6.2)$$

Note that

$$\nabla^2 \psi = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) + \frac{1}{r^2} \left( \frac{\partial^2 \psi}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right)$$

and

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

So we can also write

$$\nabla^2 \psi = \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) - \frac{1}{r^2 \hbar^2} \hat{\mathbf{L}}^2 \psi \quad (6.3)$$

Substituting into equation (6.1), using equation (6.2), we get

$$\begin{aligned} & -\frac{\hbar^2}{2m} \nabla^2 R(r) Y_{\ell, m_\ell} \\ &= -\frac{\hbar^2}{2mr} \frac{\partial^2}{\partial r^2} (rR(r) Y_{\ell, m_\ell}(\theta, \phi)) + \frac{1}{2mr^2} \hat{\mathbf{L}}^2 (R(r) Y_{\ell, m_\ell}(\theta, \phi)) \\ &= -\frac{\hbar^2}{2mr} \frac{\partial^2}{\partial r^2} (rR(r) Y_{\ell, m_\ell}(\theta, \phi)) + \frac{1}{2mr^2} R(r) \ell(\ell+1) \hbar^2 Y_{\ell, m_\ell}(\theta, \phi) \\ &= ER(r) Y_{\ell, m_\ell}(\theta, \phi) - V(r) R(r) Y_{\ell, m_\ell}(\theta, \phi) \end{aligned}$$

Here we can remove the spherical harmonic  $Y_{\ell, m_\ell}(\theta, \phi)$  and multiply by  $r$  to get

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} (rR(r)) + \frac{\ell(\ell+1) \hbar^2}{2mr^2} rR(r) + V(r) rR(r) = ErR(r)$$

If we set  $u(r) = rR(r)$ , we can rewrite

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} u(r) + \left[ \frac{\ell(\ell+1) \hbar^2}{2mr^2} + V(r) \right] u(r) = Eu(r)$$

Here we will get eigenfunctions  $u_{n_r, \ell}(r)$  with energy  $E_{n_r, \ell}$  and therefore

$$\psi_{n_r, \ell, m}(r, \theta, \phi) = \frac{u_{n_r, \ell}(r)}{r} Y_{\ell m}(\theta, \phi)$$

which must be an eigenfunction of  $\hat{H}$ ,  $\hat{L}_z$ ,  $\hat{\mathbf{L}}^2$ .

Introduce the *parity* of a wave function

$$\psi(-\mathbf{r}) = \pm \psi(\mathbf{r})$$

The eigenvalues are +1 (even parity) and -1 (odd parity). In a central potential, the parity is even if  $\ell$  is even and it is odd, if  $\ell$  is odd. The parity is an observable and the parity operator eigenvalues are  $\pm 1$ .  $\hat{H}$  and the parity operator commute if  $\hat{H}(-\mathbf{r}) = H(\mathbf{r})$ .

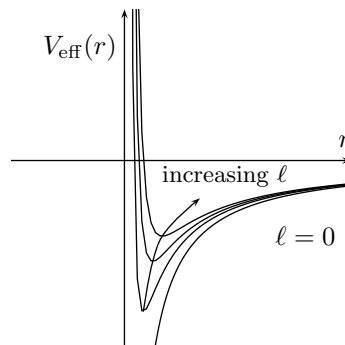
### 6.3 Hydrogen atom

We would like to solve the radial Schrödinger Equation

$$-\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial r^2} u_{n_r, \ell} + \frac{\ell(\ell+1) \hbar^2}{2m_e r^2} u_{n_r, \ell} - \frac{e^2}{4\pi\epsilon_0 r} u_{n_r, \ell} = E_{n_r, \ell} u_{n_r, \ell}$$

with  $u \rightarrow 0$  as  $r \rightarrow 0$  (because  $\psi$  is finite at  $r = 0$ ) and as  $r \rightarrow \infty$ . We define the *effective potential*

$$V_{\text{eff}}(r) := \frac{\ell(\ell+1) \hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r}$$



The minimum, we get by

$$\frac{dV_{\text{eff}}}{dr} = -\frac{\ell(\ell+1)\hbar^2}{m_e r^3} + \frac{e^2}{4\pi\epsilon_0 r^2} = 0$$

where

$$r = r_{\min} = \ell(\ell+1)\hbar^2 \frac{4\pi\epsilon_0}{m_e e^2} =: \ell(\ell+1)a_0$$

and  $a_0$  is the *Bohr radius*

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} = 0.53 \cdot 10^{-10} \text{m}$$

For the energy at  $r_{\min}$  we get

$$V_{\text{eff}}(\ell(\ell+1)a_0) = -\frac{1}{2} \frac{e^2}{e\pi\epsilon_0 a_0} \frac{1}{\ell(\ell+1)} = -\frac{E_R}{\ell(\ell+1)}$$

where  $E_R$  is the *Rydberg energy*

$$E_R := \frac{e^2}{8\pi\epsilon_0 a_0} = 136 \text{eV}$$

For high  $\ell$ , we have a high energy and the probability gets further out. Introduce the *fine structure constant*

$$\alpha := \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.035\dots}$$

which is a dimensionless constant. Now

$$a_0 = \frac{1}{\alpha} \frac{\hbar}{m_e c} \quad E_R = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{\alpha^2}{2} m_e c^2$$

and we solve

$$-\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial r^2} u_{n_r, \ell} + \left( \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) u_{n_r, \ell} = E_{n_r, \ell} u_{n_r, \ell}$$

Setting  $r = qa_0$ ,  $E = -\gamma^2 E_R$ , we can write this as

$$\frac{\partial^2 u}{\partial q^2} + \left( \frac{2}{q} - \frac{\ell(\ell+1)}{q^2} \right) u = \gamma^2 u \quad (6.4)$$

We have the boundary conditions  $u(q) = 0$  at  $q = 0$  and as  $q \rightarrow \infty$ . Then, at large  $q$ , we get the equation

$$\frac{d^2 u}{dq^2} = \gamma^2 u$$

which has the general solutions

$$u(q) = Ae^{-\gamma q} + Be^{\gamma q} = Ae^{-\gamma q}$$

where we set  $B = 0$ , because  $u(q) \rightarrow 0$  as  $q \rightarrow \infty$ . For small  $q$ , we get

$$\frac{d^2 u}{dq^2} - \frac{\ell(\ell+1)u}{q^2} = 0$$

which has solutions

$$u(q) = Aq^{\ell+1} \quad \text{or} \quad u(q) = Bq^{-\ell}$$

where the second one wouldn't satisfy  $u(q) = 0$  at  $q = 0$ . So we look for

$$u(q) = f(q)q^{\ell+1}e^{-\gamma q}$$

which (by substituting into equation (6.4)) leads to

$$q \frac{d^2 f}{dq^2} + 2[(\ell + 1) - \gamma q] \frac{df}{dq} + 2[1 - \gamma(\ell + 1)] f = 0$$

This has solutions

$$f(q) = p_{n_r, \ell}(q) = \sum_s a_s q^s$$

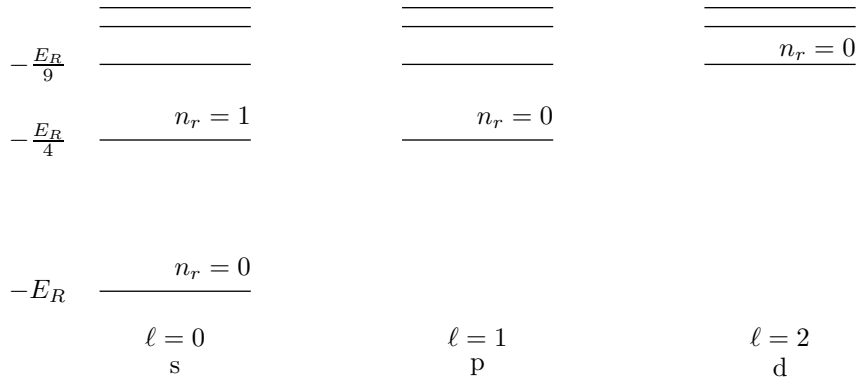
with

$$a_{s+1} = \left[ \frac{2\gamma(s + \ell + 1) - 2}{s(s + 1) + 2(s + 1)(\ell + 1)} \right] a_s \quad \gamma = \frac{1}{n_r + \ell + 1}$$

so that  $p_{n_r, \ell}(r)$  terminates at  $a_{n_r} q^{n_r}$ . Finally, we get

$$u_{n_r, \ell}(r) = N p_{n_r, \ell}(r) r^{\ell+1} e^{-\frac{r}{a_0(n_r + \ell + 1)}} \quad E_{n_r, \ell} = -\frac{E_R}{(n_r + \ell + 1)^2}$$

For each  $\ell$ , there is an infinite number of discrete energy states as  $n_r$  goes from 0 to  $\infty$ .



## 6.4 Zeeman effect - Perturbing the Hamiltonian $\hat{H}$

We introduce the total angular momentum as the sum of the orbital angular momentum and the spin. We had before

$$\begin{aligned} L &= \sqrt{\ell(\ell + 1)} \hbar & m_\ell &= -\ell, -\ell + 1, \dots, \ell \\ S &= \sqrt{s(s + 1)} \hbar & m_s &= -s, -s + 1, \dots, s \end{aligned}$$

Now, we add

$$J = \sqrt{j(j + 1)} \hbar \quad m_j = -j, -j + 1, \dots, +j$$

The question now is, how to get  $j$  from  $\ell$  and  $s$ . The possible values of  $j$  range from  $j = \ell + s$  and  $j = |\ell - s|$  with  $\Delta j = 1$ . e.g. if we have  $\ell = 2$ ,  $s = \frac{1}{2}$ , then  $j = \frac{5}{2}$  or  $j = \frac{3}{2}$  and therefore

$$m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \dots, \frac{5}{2} \quad \text{or} \quad m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$$

We also dealt earlier with the magnetic moment, which depends on whether the angular momentum is coming from spin or orbital angular momentum and so we can write general formulae

$$\boldsymbol{\mu} = I \mathbf{A} = \frac{q}{2m} \mathbf{L} \quad \mu_z = -g \frac{e}{2m_e} \hbar m_j$$

This  $g$  here is called the *Landé g factor*, which is given by

$$g = 1 + \frac{j(j + 1) - \ell(\ell + 1) + s(s + 1)}{2j(j + 1)}$$

so  $g = 1$  if  $s = 0$  and  $g = 2$  if  $\ell = 0$ . Now we can consider an atom placed in a magnetic field. The electron acquires energy

$$E_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B}$$

If we have arranged things, so that  $|\mathbf{B}| = B_z$ , then

$$E_{\text{mag}} = -\mu_z B = g\mu_B m_j B \quad \mu_B = \frac{e\hbar}{2m_e}$$

where  $\mu_B$  is the Bohr magneton. We had

$$\hat{H}\psi_{n_r, \ell, m} = E\psi_{n_r, \ell, m} \quad \hat{H} = \hat{H}_0 + \underbrace{m_j g \mu_B B}_{\text{const}}$$

The effect is, that all energy levels are split into  $2j + 1$  components. This is called the *Zeeman effect*.

## 6.5 Time-dependent perturbations - Radiative transitions

If  $\hat{H}$  changes with time, we get transitions between “stationary states”. Imagine the unperturbed eigenfunctions  $\Psi_k^0$  and eigenvalues  $\varepsilon_k^0$ . In this case, we have the time-independent form of the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi_k^0(t) = \hat{H}_0 \Psi_k^0(t) = \varepsilon_k^0 \Psi_k^0(t)$$

We’d expect then, that the general solution of this is a superposition

$$\Psi^0(t) = \sum_k a_k^0 \Psi_k^0(t) = \sum_k a_k^0 e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \psi_k^0$$

Now we perturb  $\hat{H} = \hat{H}_0 + \hat{V}(t)$ . We can write

$$i\hbar \frac{\partial}{\partial t} \Psi(t) = (\hat{H}_0 + \hat{V}(t)) \Psi(t)$$

Assume that

$$\Psi(t) = \sum_k a_k(t) \Psi_k^0(t) = \sum_k a_k(t) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \psi_k^0$$

and substitute into the Schrödinger equation

$$i\hbar \sum_k \left( \frac{da_k(t)}{dt} - \frac{i\varepsilon_k^0}{\hbar} a_k(t) \right) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \psi_k^0 = \sum_k (\varepsilon_k^0 + \hat{V}(t)) a_k(t) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \psi_k^0$$

which can be simplified to

$$i\hbar \sum_k \left( \frac{da_k(t)}{dt} \right) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \psi_k^0 = \sum_k \hat{V}(t) a_k(t) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \psi_k^0$$

Now we multiply by another state  $\psi_n^{0*}$  and integrate over  $d^3\mathbf{r}$

$$i\hbar \sum_k \left( \frac{da_k(t)}{dt} \right) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \underbrace{\int \psi_n^{0*} \psi_k^0 d^3\mathbf{r}}_{\delta_{nk}} = \sum_k a_k(t) e^{-\frac{i\varepsilon_k^0 t}{\hbar}} \int \psi_n^{0*} \hat{V} \psi_k^0 d^3\mathbf{r}$$

and it follows

$$i\hbar \frac{d}{dt} a_n(t) = \sum_k a_k(t) e^{i(\varepsilon_n^0 - \varepsilon_k^0) \frac{t}{\hbar}} \int \psi_n^{0*} \hat{V} \psi_k^0 d^3\mathbf{r}$$

If we assume that the initial state were an eigenfunction  $\psi_j$ , we get

$$i\hbar \frac{d}{dt} a_n(t) = \int \psi_n^{0*} \hat{V} \psi_j^0 d^3\mathbf{r} e^{i(\varepsilon_n^0 - \varepsilon_j^0) \frac{t}{\hbar}}$$

and therefore

$$a_n(t) = -\frac{i}{\hbar} \int_0^t \int \psi_n^{0*} \hat{V} \psi_j^0 d^3\mathbf{r} e^{i(\varepsilon_n^0 - \varepsilon_j^0) \frac{t'}{\hbar}} dt'$$

where we define

$$V_{nj} := \int \psi_n^{0*} \hat{V} \psi_j^0 d^3\mathbf{r} \quad \varepsilon_{nj} := \varepsilon_n^0 - \varepsilon_j^0$$

If the perturbation is constant and applied for some time  $t$ , we can write

$$\begin{aligned} a_n(t) &= -\frac{i}{\hbar} V_{nj} \int_0^t e^{i\varepsilon_{nj} \frac{t'}{\hbar}} dt' = -\frac{i}{\hbar} V_{nj} \left( \frac{\hbar}{i\varepsilon_{nj}} e^{i\varepsilon_{nj} \frac{t'}{\hbar}} \right) \Big|_0^t \\ &= -\frac{V_{nj}}{\varepsilon_{nj}} \left( e^{i\varepsilon_{nj} \frac{t}{\hbar}} - 1 \right) \end{aligned}$$

Define

$$P_{jn} := |a_n(t)|^2 = \frac{|V_{nj}|^2}{\varepsilon_{nj}^2} 4 \sin^2 \left( \frac{\varepsilon_{nj} t}{2\hbar} \right)$$

where as  $t \rightarrow \infty$

$$\frac{\sin^2 \left( \frac{\varepsilon_{nj} t}{2\hbar} \right)}{t \varepsilon_{nj}^2}$$

behaves as  $\frac{\pi}{2\hbar} \delta(\varepsilon_{nj})$ , that is

$$\rightarrow \lim_{t \rightarrow \infty} \frac{P_{jn}(t)}{t} = \frac{2\pi}{\hbar} |V_{nj}|^2 \delta(\varepsilon_{nj})$$

If  $\hat{V}$  is time varying, we cannot take outside of the integral  $\int dt'$ , e.g. the  $\mathbf{E}$ -wave is interacting with the dipole of the atom, e.g.

$$\hat{V} = (e\hat{\mathbf{r}})E_0 \cos \omega t$$

where  $e\hat{\mathbf{r}}$  is the dipole of the atom. So it is exactly as before, but now

$$\delta \rightarrow \delta(\varepsilon_{nj} \pm \hbar\omega)$$

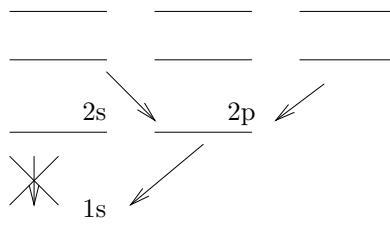
and the transition probability is

$$\lim_{t \rightarrow \infty} \frac{P_{jn}(t)}{t} = \frac{2\pi}{\hbar} |V_{nj}|^2 |A(\omega_{nj})|^2$$

where  $|A(\omega)|^2$  is the strength of perturbation at  $\omega = \frac{\varepsilon_{nj}}{\hbar}$ . We only get transitions, if  $\hbar\omega = |\varepsilon_{nj}|$  and  $|V_{nj}|^2 \neq 0$ . The interaction with the dipole of the atom is proportional to  $\hat{\mathbf{r}}$  which is the operator of  $\mathbf{r}$  and not the unit vector. Look at

$$\int \psi_n \hat{\mathbf{r}} \psi_j d^3\mathbf{r}$$

Note that the operator  $\hat{\mathbf{r}}$  changes sign when  $\mathbf{r} \rightarrow -\mathbf{r}$ , therefore  $V_{nj} = 0$  unless  $\psi_n$  and  $\psi_j$  have opposite parity.



## 6.6 Some (small) complicating effects

So far, we have considered  $\hat{H}$

- non-relativistic
- only with Coulomb forces
- assuming, that the mass of the proton was  $\infty$ .

### 6.6.1 The reduced mass effect

The mass of the proton  $m_p$  is not  $\infty$  and therefore the proton and the electron orbit around a common center of mass. The energy is

$$E = \frac{p_e^2}{2m_e} + \frac{p_p^2}{2m_p} - \frac{e^2}{4\pi\epsilon_0 r}$$

In the center of mass frame, we have  $p_e = p_p = p$  and

$$E = \frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r} \quad \mu = \frac{m_e m_p}{m_e + m_p}$$

where  $\mu$  is the *reduced mass*. The net effect of this is to change the length and energy scales

$$a'_0 = \frac{m_e}{\mu} a_0 \quad E'_R = \frac{\mu}{m_e} E_R \quad E'_n = \frac{\mu}{m_e} E_n$$

For the electron-proton atom (i.e. Hydrogen  $^1H$ ), we have

$$\frac{\mu}{m_e} = \frac{1836}{1837}$$

or for Deuterium  $^2H$  ( $e^-$  and  $p^+ n^0$ ) we get

$$\frac{\mu}{m_e} = \frac{3671}{3672}$$

### 6.6.2 Spin-orbit coupling

This is a modification of  $\hat{H}$  due to the magnetic field produced by the orbital motion interacting with  $\mu$  from the spin. The electron sees an “orbiting” proton with period

$$\tau = \frac{2\pi r}{v} = 2\pi \frac{m_e r^2}{L_e}$$

This means, that effectively we have a current

$$I = \frac{e}{\tau} \Rightarrow B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{e L_e}{2\pi m_e r^2} = \frac{e}{4\pi\epsilon_0 m_e c^2 r^3} L_e$$

and we have

$$\mu_e = -2 \frac{e}{2m_e} \mathbf{S}$$

and therefore

$$E_{\text{mag}} = -\boldsymbol{\mu} \cdot \mathbf{B} = \frac{e^2}{4\pi\epsilon_0 m_e^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S}$$

This isn't completely correct. Correct would be

$$E_{\text{mag}} = \frac{e^2}{8\pi\epsilon_0 m_e^2 c^2 r^3} \mathbf{L} \cdot \mathbf{S}$$

where  $L \sim S \sim \hbar$  and

$$E_{\text{mag}} \sim \frac{e^2 \hbar^2}{4\pi\epsilon_0 m_e^2 c^2 a_0^3} = \alpha^4 m_e c^2$$

### 6.6.3 Relativist effects

We know the relativistic energy

$$\varepsilon = \sqrt{m_e^2 c^4 + p^2 c^2} = m_e c^2 + \frac{p^2}{2m_e} - \frac{1}{8} \left( \frac{p}{m_e c} \right)^4 m_e c^2 + \dots$$

where  $p^2 = E 2m_e \sim \alpha^2 m_e^2 c^2$  and therefore  $p \sim \alpha m_e c$ . This means that the relativistic correction is of order

$$\varepsilon = \frac{\alpha^4}{8} m_e c^2$$



## 7 Quantum mechanics of identical particles

In deterministic Classical Physics we keep track of even identical particles. In Quantum Physics it is probabilistic, so it's impossible to keep track of individual particles.

### 7.1 Wave functions for identical particles

Consider two particles  $p, q$ , then we have a “2-particle wave-function”

$$\Psi(\mathbf{r}_p, \mathbf{r}_q, t)$$

The probability of finding  $p$  at  $\mathbf{a}$  and  $q$  at  $\mathbf{b}$  is

$$|\Psi(\mathbf{a}, \mathbf{b}, t)|^2 d^3\mathbf{a} d^3\mathbf{b}$$

If we have two identical particles, we get

$$|\Psi(\mathbf{a}, \mathbf{b}, t)|^2 = |\Psi(\mathbf{b}, \mathbf{a}, t)|^2$$

This enables us to say that

$$\Psi(\mathbf{a}, \mathbf{b}, t) = e^{i\delta} \Psi(\mathbf{b}, \mathbf{a}, t)$$

where  $e^{-i\delta}$  can be a “phase factor”. Then

$$\Psi(\mathbf{a}, \mathbf{b}, t) = e^{2i\delta} \Psi(\mathbf{a}, \mathbf{b}, t) \Rightarrow e^{i\delta} = \pm 1$$

Therefore, the wave function of two identical particles must be symmetric or anti-symmetric under exchange of  $p$  and  $q$ . Later, the symmetric ones, we will call *Bosons* and the anti-symmetric ones *Fermions*.

Take the Hamiltonian of the harmonic oscillator, assuming that  $p$  and  $q$  do not depend on each other

$$\hat{H}(\mathbf{x}_p, \mathbf{x}_q) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}_p^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{x}_q^2} + \frac{1}{2} m\omega^2 \mathbf{x}_p^2 + \frac{1}{2} m\omega^2 \mathbf{x}_q^2$$

The eigenfunctions are  $\psi_n$  with  $E_n = (n + \frac{1}{2}) \hbar\omega$

- 1) If  $p$  and  $q$  are in exactly the same state ( $n_q = n_p$ ), we get

$$E = 2E_n = (2n + 1) \hbar\omega$$

and the wave-function

$$\Psi(\mathbf{x}_p, \mathbf{x}_q, t) = \psi_n(\mathbf{x}_p) \psi_n(\mathbf{x}_q) e^{-i(2E_n)t/\hbar}$$

Verify that it is a solution of

$$\hat{H}\Psi(\mathbf{x}_p, \mathbf{x}_q, t) = E\Psi(\mathbf{x}_p, \mathbf{x}_q, t)$$

In this case,  $\Psi$  is symmetric under the  $p$  to  $q$  exchange operator. We can not find an anti-symmetric solution, if  $p$  and  $q$  are in the same state.

- 2) If  $p$  and  $q$  are in different states and also distinguishable (denoted by  $D$  superscript), we will have

$$E = E_n + E_{n'} = (n + n' + 1) \hbar\omega$$

We can construct two solutions

$$\begin{aligned} \Psi_1^D(\mathbf{x}_p, \mathbf{x}_q, t) &= \psi_n(\mathbf{x}_p) \psi_{n'}(\mathbf{x}_q) e^{-i(E_n + E_{n'})t/\hbar} \\ \Psi_2^D(\mathbf{x}_p, \mathbf{x}_q, t) &= \psi_n(\mathbf{x}_q) \psi_{n'}(\mathbf{x}_p) e^{-i(E_n + E_{n'})t/\hbar} \end{aligned}$$

and any linear combination will be a solution. In particular, we can write

$$\Psi^D(\mathbf{x}_p, \mathbf{x}_q, t) = c_1 \Psi_1^D(\mathbf{x}_p, \mathbf{x}_q, t) + c_2 \Psi_2^D(\mathbf{x}_p, \mathbf{x}_q, t)$$

where  $|c_1|^2$  is the probability that  $p$  is in state  $n$  and  $q$  in state  $n'$  and  $|c_2|^2$  is the probability that  $q$  is in state  $n$  and  $p$  in state  $n'$ .

3) If we have  $n$  and  $n'$  but  $p$  and  $q$  are now indistinguishable, then

$$|c_1|^2 = |c_2|^2 = \frac{1}{2}$$

Now we can construct symmetric and anti-symmetric wave functions

$$\begin{aligned}\Psi^S(\mathbf{x}_p, \mathbf{x}_q, t) &= \frac{1}{\sqrt{2}} (\psi_n(\mathbf{x}_p)\psi_{n'}(\mathbf{x}_q) + \psi_n(\mathbf{x}_q)\psi_{n'}(\mathbf{x}_p)) e^{-i(E_n+E_{n'})\frac{t}{\hbar}} \\ \Psi^A(\mathbf{x}_p, \mathbf{x}_q, t) &= \frac{1}{\sqrt{2}} (\psi_n(\mathbf{x}_p)\psi_{n'}(\mathbf{x}_q) - \psi_n(\mathbf{x}_q)\psi_{n'}(\mathbf{x}_p)) e^{-i(E_n+E_{n'})\frac{t}{\hbar}}\end{aligned}$$

Its interesting to look at  $\Psi^D$ ,  $\Psi^S$ ,  $\Psi^A$  for  $\mathbf{x}_p = \mathbf{x}_q = \mathbf{x}_0$ . We find

$$\begin{aligned}\Psi^D(\mathbf{x}_0, \mathbf{x}_0, t) &= \psi_n(\mathbf{x}_0)\psi_{n'}(\mathbf{x}_0)e^{-i(E_n+E_{n'})\frac{t}{\hbar}} \\ \Psi^S(\mathbf{x}_0, \mathbf{x}_0, t) &= \sqrt{2}\psi_n(\mathbf{x}_0)\psi_{n'}(\mathbf{x}_0)e^{-i(E_n+E_{n'})\frac{t}{\hbar}} \\ \Psi^A(\mathbf{x}_0, \mathbf{x}_0, t) &= 0\end{aligned}$$

This means, that relative to the case of distinguishable particles, we can say that the symmetric  $\Psi^S$  is twice as likely to have both particles in the same place at the same time and the anti-symmetric  $\Psi^A$  never has the two particles in the same place at the same time. For examples, see the exercise sheet.

## 7.2 Exchange symmetry with spin

Recall that we had the spin angular momentum  $S = \sqrt{s(s+1)}\hbar$  with  $z$ -component  $S_z = m_s\hbar$ . Lets say, we have a spin wave function  $\chi(p)$  with

$$\chi(p) = \sum_{m_s=-s}^s c_{m_s}\chi_{s,m_s}(p)$$

We can combine this with the (normal) spatial wave function  $\psi$ , to get

$$\Phi_{n,\ell,m_\ell,s,m_s} = \psi_{n,\ell,m_\ell}\chi_{s,m_s}$$

Now look at two indistinguishable particles in exactly the same state. We will again find a wave function

$$\Phi(p, q) = \Phi_{n,\ell,m_\ell,s,m_s}(p)\Phi_{n,\ell,m_\ell,s,m_s}(q)$$

and again,  $\Psi^A$  for the same states does not exist.

But what about particles in different states? Can we represent the wave function as product of two single particle states?

$$\begin{aligned}\Psi^S(p, q) &= \frac{1}{\sqrt{2}} \left( \Phi_{n,\ell,m_\ell,s,m_s}(p)\Phi_{n',\ell',m'_\ell,s',m'_s}(q) + \Phi_{n,\ell,m_\ell,s,m_s}(q)\Phi_{n',\ell',m'_\ell,s',m'_s}(p) \right) \\ \Psi^A(p, q) &= \frac{1}{\sqrt{2}} \left( \Phi_{n,\ell,m_\ell,s,m_s}(p)\Phi_{n',\ell',m'_\ell,s',m'_s}(q) - \Phi_{n,\ell,m_\ell,s,m_s}(q)\Phi_{n',\ell',m'_\ell,s',m'_s}(p) \right)\end{aligned}$$

which is exactly the same approach as we had before. But we could also have the product of two two-particle states as

$$\begin{aligned}\Phi^{2,S}(p, q) &= \psi^S(p, q)\chi^S(p, q) \\ \Phi^{2,A}(p, q) &= \psi^A(p, q)\chi^S(p, q) \\ \Phi^{2,A}(p, q) &= \psi^S(p, q)\chi^A(p, q) \\ \Phi^{2,S}(p, q) &= \psi^A(p, q)\chi^A(p, q)\end{aligned}$$

**Example 7.1:** Consider two particles with  $s_1, s_2 = \frac{1}{2}$  and remember that if we have the combination of two spin-numbers  $s_1, s_2$  then  $S = |s_1 - s_2|, \dots, s_1 + s_2$ . Therefore, we get  $S = 1 = s_1 + s_2$  with  $m_S = -1, 0, 1$  or  $S = 0 = |s_1 - s_2|$  with  $m_S = 0$ . Lets call  $\chi_{\frac{1}{2}, +\frac{1}{2}} = \chi_+$  and  $\chi_{\frac{1}{2}, -\frac{1}{2}} = \chi_-$ , then

$$\begin{aligned}\chi_{1,1}^S(p, q) &= \chi_+(p)\chi_+(q) \\ \chi_{1,0}^S(p, q) &= \frac{1}{\sqrt{2}}(\chi_+(p)\chi_-(q) + \chi_+(q)\chi_-(p)) \\ \chi_{1,-1}^S(p, q) &= \chi_-(p)\chi_-(q) \\ \chi_{0,0}^A(p, q) &= \frac{1}{\sqrt{2}}(\chi_+(p)\chi_-(q) - \chi_+(q)\chi_-(p))\end{aligned}$$

□

As we already mentioned, the nature gives us then two types of particles, namely Bosons (photon,  ${}^4\text{He}$ , ...) and Fermions ( $e^-$ ,  $p^+$ ). Lets simply state the rules: The exchange symmetry depends on the spin of the particle. In particular, particles with integer total spin must have a symmetric wave function under particle exchange. Particles with half integer spin must have anti-symmetric two-particle wave-functions under the action of changing the two particles. The Bosons have integer spin and therefore a symmetric  $\Psi$ . The Fermions have half integer spin and therefore an anti-symmetric  $\Psi$ .

*Consequences for Fermions:*

- 1) Two Fermions (e.g. two electrons) can never have absolutely identical quantum states, because we can only make symmetric  $\Psi^S$  out of identical wave functions.
- 2) When the two-particle spin state is anti-symmetric  $\chi^A$ , then  $\Psi$  must be symmetric  $\Psi^S$ . This means, that the “electrons like to be together”. We call it *Covalent Bond*.
- 3) When the spin is symmetric  $\chi^S$ , then  $\Psi$  must be anti-symmetric, which means that the electrons are never together. We call this *rigidity of matter*.

*Consequences for Bosons:* We can always make symmetric wave-functions from two or more identical states. This is used by Lasers, the Bose-Einstein Condensate and superfluidity.

## 8 More Complicated Atoms

For more complicated atoms, we'll have to modify what we've got for the H-atom. Multiple  $e$  atoms will have a Hamiltonian  $H$  that includes the term due to the electron-electron interaction, e.g. for He we have

$$H = -\frac{\hbar^2}{2m} (\nabla_p^2 + \nabla_q^2) + V(\mathbf{r}_p, \mathbf{r}_q)$$

where

$$V(\mathbf{r}_p, \mathbf{r}_q) = -\frac{2e^2}{4\pi\epsilon_0 r_p} - \frac{2e^2}{4\pi\epsilon_0 r_q} + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_p - \mathbf{r}_q|}$$

with two's in the first two terms, because the nucleus has order  $Z = 2$ . What we do, to deal with those more complicated atoms is to modify the central potential. Close to the nucleus, the potential is something like

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Very far away, we could take

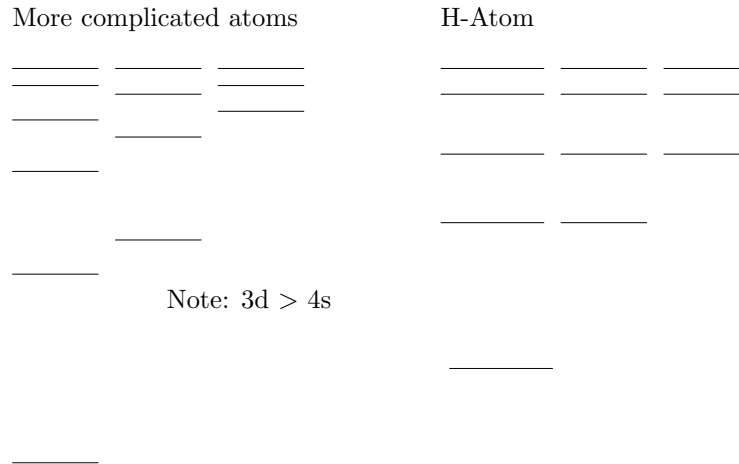
$$V(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

We combine these two potentials by

$$V(r) = z(r) \frac{-e^2}{4\pi\epsilon_0 r} \quad z(r) = ((z-1)e^{-\frac{r}{a}} + 1) \quad a = \frac{1}{2}a_0$$

Therefore, we solve for a single electron to get the eigenfunctions. Once we've got the eigenfunctions, we can "populate" them with the electrons. Then there are two changes:

- At low  $n$ , the energy eigenvalues are much lower (by a factor of  $z^2$ , where one  $z$  is because of the potential  $V(r)$  and the other  $z$  because of  $a_0 \propto \frac{1}{z}$ ).
- The degeneracy between  $\ell$  states is broken



Note: 3d > 4s

Now assign electrons to these  $n, \ell, m$  states, 2 at a time ( $\uparrow\downarrow$ ), to get

- 1s:  $n = 1, \ell = 0, m = 0 \Rightarrow 2$  electrons
- 2s:  $n = 2, \ell = 0, m = 0 \Rightarrow 2$  electrons
- 2p:  $n = 2, \ell = 1, m = -1, 0, 1 \Rightarrow 6$  electrons
- 3s:  $n = 3, \ell = 0, m = 0 \Rightarrow 2$  electrons
- 3p:  $n = 3, \ell = 1, m = -1, 0, 1 \Rightarrow 6$  electrons
- 3d:  $n = 3, \ell = 2, m = -2, -1, 0, 1, 2 \Rightarrow 10$  electrons

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