Quantum Mechanics

Lecture Notes

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Vorbemerkung

Ohne es selbst untersucht zu haben oder entsprechende Untersuchungen zu kennen, wage ich die Behauptung, dass Vorworte die am gründlichsten gelesenen Seiten von Skripten, Monographien und Büchern sind. Im vorliegenden Fall, das weiß ich ganz sicher, ist der einzig akzeptable Grund dafür, dass nur hier einige zusammenhängende (deutsche) Sätze zu finden sind. Das Skript selbst besteht weitgehend aus Formeln und (englischen) Stichpunkten. Das reflektiert meine Überzeugung, dass man Quantenmechanik nicht versuchen sollte zu lernen, ohne eines oder mehrere der reichlich vorhandenen hervorragenden Lehrbücher zu Rate zu ziehen. Dieses Skript soll nicht mit diesen (teilweise recht umfangreichen) Büchern konkurrieren, sondern lediglich eine Orientierung liefern, was die Kernaussagen der Quantenmechanik sind, die in einer einsemestrigen Vorlesung typischerweise behandelt werden. Ich selbst habe eine entsprechende Vorlesung an der TU Clausthal in den Wintersemestern 03/04, 04/05 und 06/07 gehalten.

Ich hoffe, das Skript wird als Leitfaden zur Nacharbeit und Prüfungsvorbereitung nützlich sein. Hinweise auf Fehler nehme ich — wie stets — gerne entgegen.

Tom Kirchner
Clausthal-Zellerfeld im Oktober 2007

Contents

Chapter 1

Introduction

Classical (theoretical) physics consists of two pillars

Matter	Radiation
particles (trajectories)	waves (fields)
Newton	Maxwell
$\rightarrow$ classical mechanics	classical electrodynamics
+ statistical mechanics	
($\rightarrow$ classical thermodynamics)	

Both pillars are relatively independent (although wave phenomena exist also for material objects, e.g. water waves)

Experiments ($\sim$1900) bring up problems:

1. 'Quantal' behavior of radiation

   $\longrightarrow$ cannot be explained by classical electrodynamics

   - Black-body radiation

     Planck$'$s hypothesis (1900) : $E_n = nh\nu\ , \quad n = 1, 2, ...$

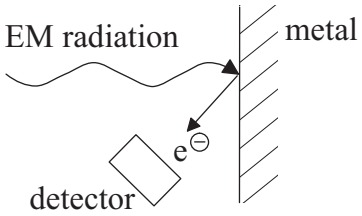
     $h = 6,626 \cdot 10^{-34}\ Js$

     $= 4,1357 \cdot 10^{-15}\ eVs$

     i.e. emission and absorption of energy is quantized

     $\longrightarrow$ Planck's law agrees with experiments

- Photoelectric effect (first experiments in 1887)



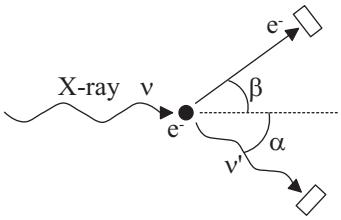
Observations:
- number of emitted electrons $\propto$ intensity of light
- kinetic energy of electrons $\propto$ frequency of light, but independent of intensity!

Einstein's interpretation (1905):
Radiation consists of photons which carry energy

$$E = h\nu$$

$\hookrightarrow$ explains observation!

- Compton effect (1922)



observation : $\nu' \leq \nu$
$\nu' = \nu'(\alpha)$

$\longrightarrow$ can be understood as inelastic collisions of 'particles'

energy of photon $E = h\nu = pc$

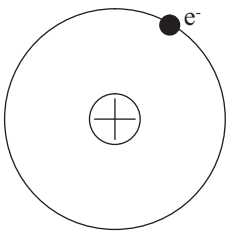
$\hookrightarrow$ momentum of photon $p = \frac{h\nu}{c} = \frac{h}{\lambda}$

2. <u>But:</u> in other situations radiation behaves like waves do (e.g. interference in Young's two-slit experiment, which in 1801/1802 was very important to establish the wave picture of radiation!)

$\longrightarrow$ dualism particle-wave

3. Structure and stability of 'atoms' (for whose existence there was ample evidence) cannot be explained by classical mechanics

- Rutherford's scattering experiment (1911) lead to 'planetary model' of an atom:



– radius of $'$nucleus$'$
$R_n \lesssim 5 \cdot 10^{-13}\ cm$
– radius of atom
$R_a \sim 10^{-8}\ cm$

but: according to classical electrodynamics these atoms cannot be stable as accelerated charges radiate and lose (continuously) energy; lifetime of Rutherford atom $\approx 10^{-11}\ s$!

- Moreover: line spectra of elements cannot be explained, but only described empirically
  (e.g. for H: Balmer/Rydberg formula:

$$\nu = R\Big(\frac{1}{m^2} - \frac{1}{n^2}\Big)\ , \qquad n, m\ \in\ N\ , \quad n > m)$$

  $\longrightarrow$ theoretical basis completely unclear!

- Bohr's model (1913):

  classical mechanics + postulates

  postulate (1): existence of stable, quantized orbits $\rightarrow$ i.e. he assumes that classical electrodynamics is not in operation on these orbits

  postulate (2): emission + absorbtion of radiation $\equiv$ transition between two orbits $h\nu = E_n - E_m$

  $\longrightarrow$ postulates + classical mechanics (and Coulomb's law) yield Balmer/Rydberg formula!

  but: problems for other atoms (He) remain and ad-hoc assumptions are not well founded

- De Broglie's matter waves (1923/24):
  Suggestion: one can ascribe wave length and frequency to a particle according to Planck's/Einstein's formulae:

$$\begin{aligned} p &= mv = \frac{h}{\lambda} \\ E &= h\nu \end{aligned}$$

  Combination of de Broglie relations with Bohr's 1^{st} postulate yields an 'interpretation' because one finds that Bohr's postulate of quantized orbits (levels) corresponds to boundary conditions of a standing wave

  $\hookrightarrow$ question: can one observe typical wave phenomena with particles?

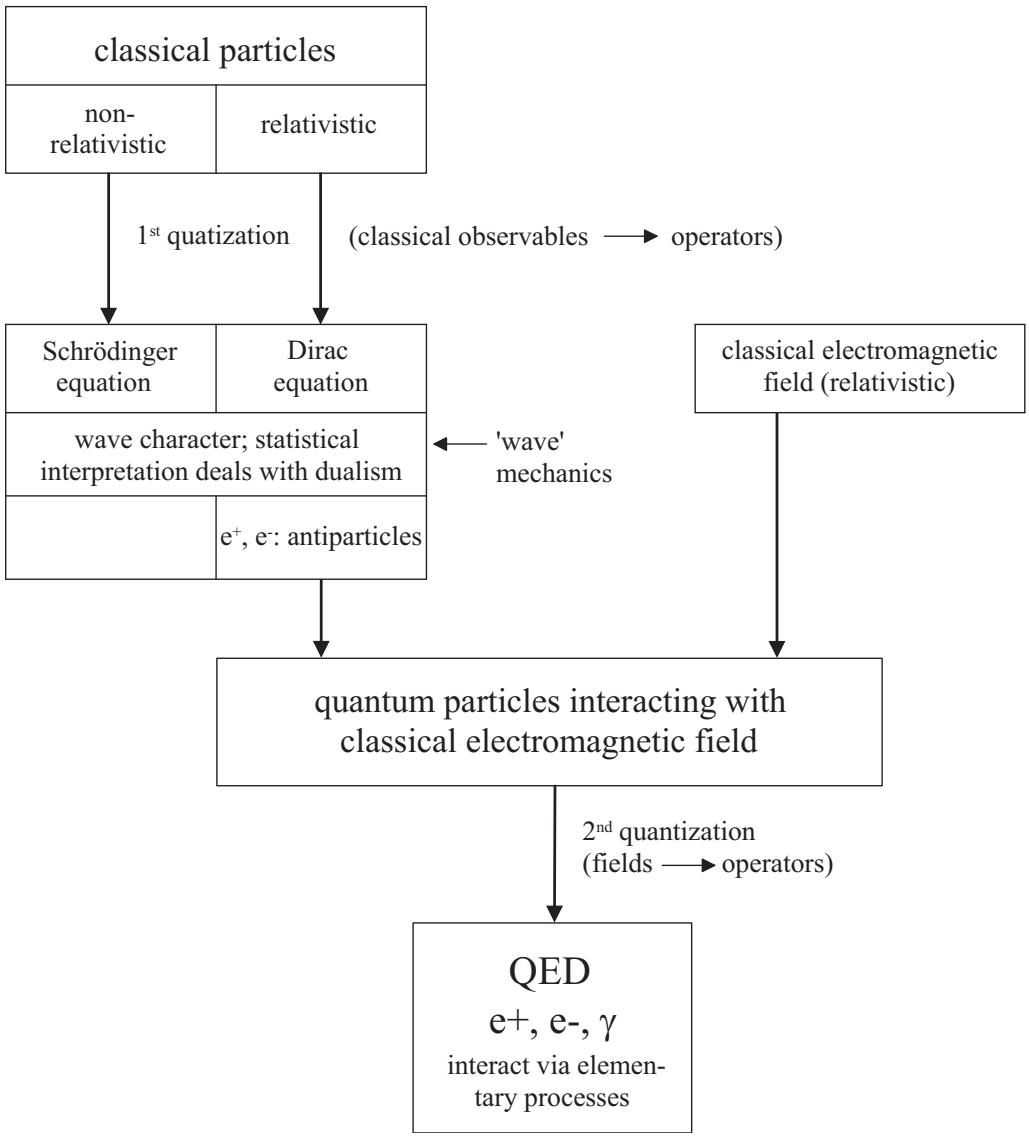
- Interference phenomena of electrons in diffraction experiments (Davisson + Germer, 1927)

$\Longrightarrow$ wave-particle dualism for radiation + matter!

bad news:	both pillars of classical theoretical physics are affected
good news:	problems are similar → solutions may be similar

⟶ in fact, one ends up with one theory instead of two; the quantum theory (QT)

A simple scheme of QT



We will be concerned mainly with the left panel (wave mechanics) in this lecture!

Chapter 2

Wave Mechanics

2.1 Matter waves

2.1.1 Classical wave functions

...solve wave equation (WE)

$$\Delta\phi - \frac{1}{v^2}\partial_{t^2}\phi = 0 \tag{2.1}$$

remember: **E** and **B** solve WE if there are no charges + currents
($\rho = 0\ , \quad \mathbf{j} = 0$)

plane waves (PWs) solve WE:

$$\phi(\mathbf{r}, t) = Ae^{i(\mathbf{kr}\pm\omega t)} \tag{2.2}$$

$$\longrightarrow \quad \omega(k) = vk \qquad \text{(dispersion relation)} \tag{2.3}$$

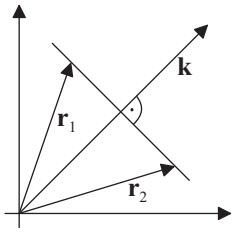
For electromagnetic (EM) waves in vaccum: $v = c \approx 3 \cdot 10^8 \frac{m}{s}$

phase of PW : $$\varphi(\mathbf{r}, \mathbf{t}) = \mathbf{kr}\pm\omega t \tag{2.4}$$

points in space with constant phase are characterized by

$$\mathbf{kr} = \text{const.} = \varphi_0 \mp \omega t_0 \tag{2.5}$$

$\boxed{t = t_0}$: eq. (2.5) defines a plane perpendicular to vector $\mathbf{k}$



$\hookrightarrow$ $-$ plane moves in direction of $\mathbf{k}$

$+$ plane moves in opposite direction

$\boxed{t > t_0}$: $\quad \varphi(\mathbf{r}, t) = \mathbf{kr} \pm \omega t \stackrel{!}{=} \varphi_0$

$\Longleftrightarrow \quad r_{\parallel}(t) = \frac{\varphi_0}{k} \mp \frac{\omega}{k} t \quad$ with $\quad r_{\parallel} = \frac{\mathbf{k} \cdot \mathbf{r}}{k}$

$$\hookrightarrow \text{ phase velocity } \quad v_{ph} = \frac{\omega}{k} \tag{2.6}$$

(consistent with eq. (2.3))

2.1.2 Transition to Matter Waves (MWs)

- Starting point: de Broglie relations

$$\omega = \frac{E}{\hbar} \ , \quad \mathbf{k} = \frac{1}{\hbar}\mathbf{p} \ , \quad (\hbar = \frac{h}{2\pi}) \tag{2.7}$$

- define a "plane matter wave", that moves in direction of $\mathbf{p}$ by using (2.7) in (2.2):

$$\phi(\mathbf{r}, t) = A e^{\frac{i}{\hbar}(\mathbf{pr} - Et)} \tag{2.8}$$

- for a free, non-relativistic particle we have

$$\mathbf{p} = m\mathbf{v}_{kl} \tag{2.9}$$

$$E = \frac{p^2}{2m} \tag{2.10}$$

use $$v_{ph} = \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{E}{p} = \frac{p}{2m} = \frac{v_{kl}}{2} \quad ? \tag{2.11}$$

  - what does that mean?
  - but concept of plane matter waves is ill-defined anyway as a particle wave needs to be localized in space!

2.1.3 Wave Packets (WPs)

defined as dense linear combinations of PWs

$$\phi(\mathbf{r},t) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int A(\mathbf{k}) e^{i(\mathbf{kr}-\omega t)}\ d^3k \tag{2.12}$$

It is easy to show that $\phi(\mathbf{r},t)$ and $A(\mathbf{k})$ form a Fourier transform pair, i.e.

$$A(\mathbf{k}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int \phi(\mathbf{r},0) e^{-i\mathbf{kr}}\ d^3r \tag{2.13}$$

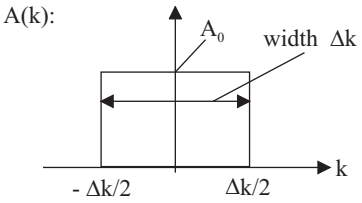
One can define a Fourier transform of $\phi(\mathbf{r},t)$ at any time t by

$$A(\mathbf{k},t) \equiv A(\mathbf{k}) e^{-i\omega t} \tag{2.14}$$

a) One-dimensional WP at $t = 0$

$$\phi(x,0) = \frac{1}{\sqrt{2\pi}} \int A(k) e^{ikx}\ dk \tag{2.15}$$

Example 1)



$$\hookrightarrow \quad \phi(x,0) = \frac{A_0}{\sqrt{2\pi}} \int_{-\frac{\Delta k}{2}}^{\frac{\Delta k}{2}} e^{ikx}\ dk = \sqrt{\frac{2}{\pi}} A_0 \frac{\sin(\frac{\Delta k}{2}x)}{x} \tag{2.16}$$

approximate width $\Delta x \approx \frac{4\pi}{\Delta k}$

$\hookrightarrow$ "classical" uncertainty (a property of Fourier transforms)

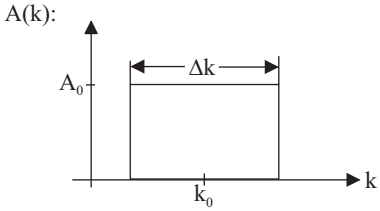
$$\Delta k \cdot \Delta x \approx 4\pi$$

define momentum width $\Delta p = \hbar \Delta k$

$$\hookrightarrow \quad \Delta x \cdot \Delta p \approx 4\pi\hbar \tag{2.17}$$

"naive uncertainty relation" (will be interpreted later on)

Example 2)



$$\begin{aligned}\phi(x,0) &= \frac{A_0}{\sqrt{2\pi}} \int_{k_0-\frac{\Delta k}{2}}^{k_0+\frac{\Delta k}{2}} e^{ikx}\, dk \\ &= \sqrt{\frac{2}{\pi}} A_0 \frac{\sin\frac{\Delta k}{2}x}{x} e^{ik_0x} \end{aligned} \tag{2.18}$$

$\hookrightarrow$ modulation of PW with wave number k_0 by envelope function

$$\chi(x,0) = \sqrt{\frac{2}{\pi}} A_0 \frac{\sin\frac{\Delta k}{2}x}{x}$$

defined via

$$\phi(x,0) = \chi(x,0)e^{ik_0x}$$

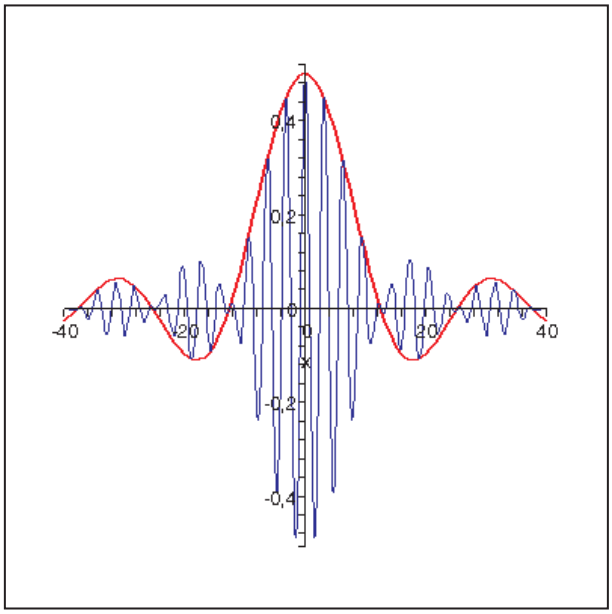


Figure 2.1: Real part of $\phi(x,0)$ (blue line) and envelope function $\chi(x,0)$ (red line)

Example 3) Gaussian wave packet (GWP)

$$\phi(x,0) = \underbrace{Ce^{-\frac{x^2}{2\Delta x^2}}}_{\text{envelope function } \chi(x,0)} e^{ik_0x} \tag{2.19}$$

width Δx (sometimes defined as $\frac{\Delta x}{\sqrt{2}}$)

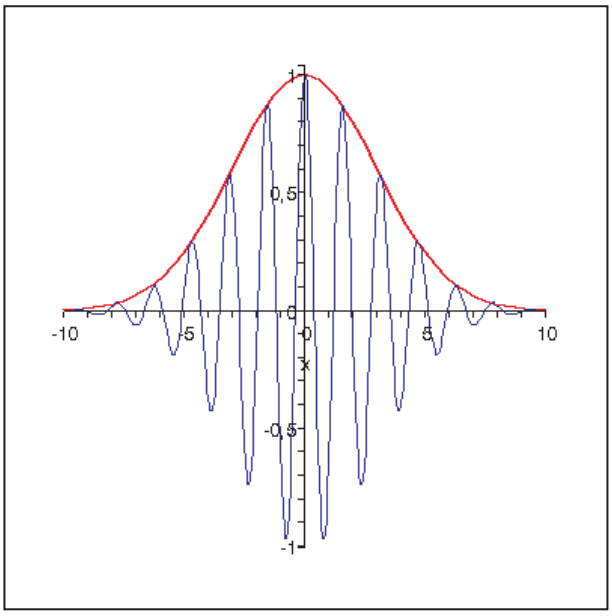


Figure 2.2: Real part of GWP (blue line) and envelope function (red line)

$$\hookrightarrow \quad A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(x,0) e^{-ikx}\, dx = \overset{\text{(exercises)}}{\ldots} =$$
$$= C\Delta x \exp\Big[-\frac{\Delta x^2 (k-k_0)^2}{2} \Big] \tag{2.20}$$

$\rightarrow$ again, this is a Gaussian! width $\Delta k = \frac{1}{\Delta x}$

$$\hookrightarrow \qquad \Delta x \cdot \Delta p \approx \hbar \tag{2.21}$$

b) Time development of WPs

define time-dependent envelope function:

$$\begin{aligned} \chi(x,t) &= \frac{1}{\sqrt{2\pi}} \int |A(k)| e^{i\varphi(k,x,t)}\, dk \\ \varphi(k,x,t) &= (k-k_0)x - (\omega(k) - \omega_0)t + \alpha(k) \\ \omega_0 &= \omega(k_0) \\ A(k) &= |A(k)| e^{i\alpha(k)} \\ \hookrightarrow \quad \phi(x,t) &= \chi(x,t) e^{i(k_0 x - \omega_0 t)} \end{aligned}$$

$\chi(x,t)$ characterizes time-development of WP "as a whole". What is the associated velocity?

$\hookrightarrow$ define center of WP via 'stationary phase condition':

$$\left.\frac{d\varphi}{dk}\right|_{k=k_0} = 0 \qquad \Longleftrightarrow \qquad x_0 = \left.\frac{d\omega}{dk}\right|_{k_0} t - \left.\frac{d\alpha}{dk}\right|_{k_0} \tag{2.22}$$

Obviously x_0 moves on a rectilinear trajectory with the constant "group velocity":

$$v_{gr} = \dot{x}_0 = \left.\frac{d\omega}{dk}\right|_{k_0}$$

Relation between group and phase velocities:

$$v_{gr} = \left.\frac{d\omega}{dk}\right|_{k_0} = \frac{d}{dk}\Big(v_{ph}\ k\Big)_{k_0} = \Big(v_{ph} + k\frac{dv_{ph}}{dk}\Big)_{k_0} \tag{2.23}$$

Example 1) EM-WP in vaccum

$$\begin{aligned} \omega(k) &= ck \\ \hookrightarrow \quad \frac{d\omega}{dk} &= c = \frac{\omega}{k} \quad \Longleftrightarrow \quad v_{gr} = v_{ph} \end{aligned}$$

In this case the shape of the WP does not change in time:

As ω is a linear function of k we can write

$$\begin{aligned} \omega(k) &= \omega_0 + \left.\frac{d\omega}{dk}\right|_{k_0} (k - k_0) \\ &= \omega_0 + v_{gr}(k - k_0) \end{aligned}$$

$$\begin{aligned} \hookrightarrow \quad \chi(x,t) &= \frac{1}{\sqrt{2\pi}} \int |A(k)| e^{i[(k-k_0)x - v_{gr}(k-k_0)t + \alpha]}\, dk \\ &= \frac{1}{\sqrt{2\pi}} \int A(k) e^{i(k-k_0)(x - v_{gr}t)}\, dk \\ &= \chi(x - v_{gr}t, 0) \end{aligned}$$

Example 2) EM-WP in media

$$\omega(k) = v_{ph}(k)k$$

in this case, ω is not a linear function of k

$$\Longrightarrow \quad \chi(x,t) \neq \chi(x - v_{gr}t, 0)$$

i.e. the WPs shape changes (dispersion)

Example 3) Matter wave packet (MWP)
(nonrelativistic case) (confer (cf.) page 6)

$$\lhd \qquad \frac{\omega}{k} = \frac{\hbar\omega}{\hbar k} = \frac{E}{p} = \frac{p}{2m} = \frac{\hbar k}{2m}$$

$$\iff \quad \omega(k) = \frac{\hbar k^2}{2m} \tag{2.24}$$

$$\hookrightarrow \quad v_{ph} = v_{ph}(k) = \frac{\omega}{k} = \frac{\hbar k}{2m} \tag{2.25}$$

$$v_{gr} = \left.\frac{d\omega}{dk}\right|_{k_0} = \frac{\hbar k_0}{m} = \frac{p_0}{m} = v_{kl} \tag{2.26}$$

$\longrightarrow$ i.e. we can identify v_{gr} with the classical velocity of the 'particle'

Since $v_{gr} \neq v_{ph}$: dispersion (in vacuum)!

How fast does the MWP disperse?

$$\begin{aligned} \lhd \qquad \omega(k) - \omega_0 &= \frac{\hbar}{2m}(k^2 - k_0^2) \\ &= \frac{\hbar}{2m}\left[(k-k_0)^2 + 2kk_0 - 2k_0^2\right] \\ &= \frac{\hbar}{2m}(k-k_0)^2 + \frac{\hbar k_0}{m}k - \frac{\hbar k_0}{m}k_0 \\ &= \frac{\hbar}{2m}(k-k_0)^2 + v_{gr}(k-k_0) \end{aligned}$$

$$\begin{aligned} \hookrightarrow \quad \chi(x,t) &= \frac{1}{\sqrt{2\pi}}\int A(k) e^{i[(k-k_0)x - (\omega-\omega_0)t]}\, dk \\ &= \frac{1}{\sqrt{2\pi}}\int A(k) e^{i[(k-k_0)(x-v_{gr}t)]} \underbrace{e^{-i\frac{\hbar}{2m}(k-k_0)^2 t}}_{\text{this term causes dispersion}} dk \end{aligned}$$

- dispersion can be neglected as long as $\frac{\hbar}{2m}(k-k_0)^2 t \ll 1$
- dispersion is significant for times

$$\tau \gtrapprox \frac{m}{\hbar}(\Delta x)^2$$

(with $\Delta x \approx \frac{1}{\Delta k} = \frac{1}{k-k_0}$)

- define width of MWP

$$\Gamma(t) = \Delta x \sqrt{1 + \left(\frac{\hbar t}{m(\Delta x)^2}\right)^2} \overset{t\to\infty}{\longrightarrow} \infty$$

spreading of MWP!

Example: GWP for $t > 0$ (cf. page 8)

$$\phi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) e^{i(kx - \frac{\hbar k^2}{2m}t)}\, dk$$

with expression (2.20) for $A(k)$

$$= \overset{\text{exercises}}{\ldots} = \text{involved complex expression!}$$

consider 'intensity' of GWP (less involved expression)

$$|\phi(x,t)|^2 = \frac{|C|^2}{\sqrt{1 + \left(\frac{\hbar t}{m\Delta x^2}\right)^2}} \exp\left[- \frac{\left(x - \frac{\hbar k_0}{m}t\right)^2}{\Delta x^2 \left(1 + \left(\frac{\hbar t}{m\Delta x^2}\right)^2\right)} \right] \tag{2.27}$$

$\longrightarrow$ still a Gaussian, centered around

$$x_0 = \frac{\hbar k_0}{m} t = v_{gr} t$$

but indeed: the width increases continuously!

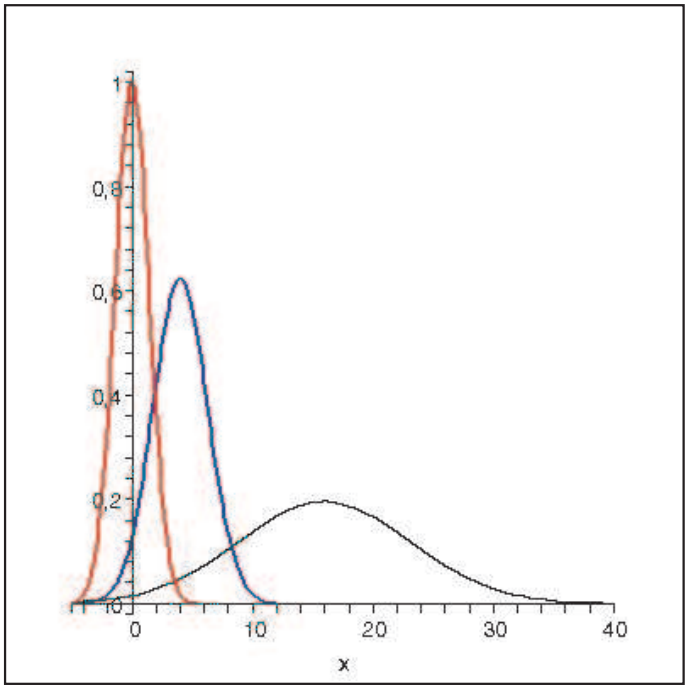


Figure 2.3: Intensity of spreading GWP at three points in time

Open questions at this point:

(a) interpretation of MWPs?

(b) is there a differential equation for MWPs?

2.2 Schrödinger equation

Some requirements for a 'matter wave equation':

- linear + homogeneous

  i.e. if eq. is solved by ψ_1, ψ_2 it is also solved by $\alpha_1\psi_1+\alpha_2\psi_2$, $(\alpha_1, \alpha_2 \in \mathbb{C})$ (principle of superposition)

- consistent with de Broglie relations

2.2.1 Schrödinger equation for a free particle

We seek for a differential equation that is solved by MWPs

- classical wave eq. (2.1)

$$\hat{D}\psi = (\Delta - \gamma\partial_{t^2})\psi = 0$$

  does not do the job!

$$\text{MWP}: \qquad \psi(\mathbf{r},t) = \int \phi(\mathbf{k},\mathbf{r},t)\; d^3k \tag{2.28}$$

$$\phi(\mathbf{k},\mathbf{r},t) = \frac{A(\mathbf{k})}{(2\pi)^{\frac{3}{2}}} \exp\Big[\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - Et)\Big] \tag{2.29}$$

$$\lhd \qquad \hat{D}\phi(\mathbf{k},\mathbf{r},t) = 0 \quad \Longleftrightarrow \quad \gamma = \frac{k^2}{\omega^2} = \frac{4m^2}{\hbar^2k^2} = \gamma(k)$$

  as γ depends on k the wave eq. is <u>not</u> solved by the MWP!

- way out: note that

$$\frac{p^2}{E} = \frac{\hbar k^2}{\omega} = 2m = \text{const.} \tag{2.30}$$

- ansatz: $\hat{D}\psi = (\Delta - \gamma\partial_t)\psi = 0$

$$\text{check}: \qquad \hat{D}\phi(\mathbf{k},\mathbf{r},t) = \Big(-\frac{p^2}{\hbar^2} + \gamma\frac{iE}{\hbar}\Big)\phi(\mathbf{k},\mathbf{r},t) = 0$$

$$\Longleftrightarrow \quad \gamma \overset{(2.30)}{=} -i\frac{2m}{\hbar} = \text{const.}$$

$$\hookrightarrow \quad \hat{D}\psi(\mathbf{r},t) = \int \hat{D}\phi(\mathbf{k},\mathbf{r},t)\; d^3k = 0$$

$\Longrightarrow$ MWP solves this differential equation: the 'free' Schrödinger equation (SE):

$$\hookrightarrow \quad -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r},t) = i\hbar\partial_t\psi(\mathbf{r},t) \tag{2.31}$$

Discussion:

- Solutions ψ must be complex
  (i.e. sin / cos -type functions do not solve (2.31))
  $\longrightarrow$ ψ is not observable!
- 'Quantization rule'
  apply SE to MWP explicitly:

$$\begin{aligned} i\hbar\partial_t\psi(\mathbf{r},t) &= \int E\frac{A(\mathbf{k})}{(2\pi)^{\frac{3}{2}}}\, e^{\frac{i}{\hbar}(\mathbf{pr}-Et)}\, d^3k \\ -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{r},t) &= \int \frac{p^2}{2m}\frac{A(\mathbf{k})}{(2\pi)^{\frac{3}{2}}}\, e^{\frac{i}{\hbar}(\mathbf{pr}-Et)}\, d^3k \end{aligned}$$

  from $i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\Delta\psi$ it follows that

$$E = \frac{p^2}{2m} \qquad \text{(classical energy conservation)}$$

  $\hookrightarrow$ extract recipe:

  – classical energy

$$E - \frac{p^2}{2m} = 0 \tag{2.32}$$

  – 'quantization'

$$\begin{aligned} E &\longrightarrow i\hbar\partial_t \equiv \hat{E} && (2.33)\\ \mathbf{p^2} &\longrightarrow -\hbar^2\triangle = \hat{\mathbf{p}}^2 && (2.34)\\ \hookrightarrow\ \mathbf{p} &\longrightarrow \frac{\hbar}{i}\bigtriangledown = \hat{\mathbf{p}} && (2.35) \end{aligned}$$

  (sign will be justified later on)

  – SE: $\left(\hat{E} - \frac{\hat{p}^2}{2m}\right)\psi = 0$

- application of the recipe to relativistic particles
  - classical energy-momentum relation

$$E^2 = \mathbf{p}^2 c^2 + m_0^2 c^4 \tag{2.36}$$

  - correspondence $E^2 \longrightarrow -\hbar^2 \partial_{t^2} \equiv \hat{E}^2$
  - $\hookrightarrow$ $(\hat{E}^2 - \hat{\mathbf{p}}^2 c^2 - m_0^2 c^4)\psi = 0$

$$\Longleftrightarrow \quad \left(\Delta - \frac{1}{c^2}\partial_{t^2} - \left(\frac{m_0 c}{\hbar}\right)^2\right)\psi(\mathbf{r}, t) = 0 \tag{2.37}$$

Klein-Gordon-equation

$\overset{m_0 \to 0}{\longrightarrow}$ classical wave equation

Looks nice, but it turns out that this equation does not work for electrons (cf. Section 5)

2.2.2 SE for a particle in a potential (conservative system)

use recipe:

- classical energy

$$E = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = \underbrace{H(\mathbf{r}, \mathbf{p})}_{\text{Hamilton function}} \tag{2.38}$$

- quantization

$$\hookrightarrow \quad (\hat{E} - \hat{H})\psi = 0 \tag{2.39}$$

$$\Longleftrightarrow \quad i\hbar\partial_t \psi(\mathbf{r}, t) = \hat{H}\psi(\mathbf{r}, t) \tag{2.40}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) \tag{2.41}$$

- note that $V(\mathbf{r})$ is not quantized (i.e. we apply the trivial quantization rule $\mathbf{r} \to \hat{\mathbf{r}} \equiv \mathbf{r}$)
- extension to time-dependent potentials $V(\mathbf{r}, t)$

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

$$\hookrightarrow \quad (\hat{E} - \hat{H}(t))\psi = 0$$

$$\iff \quad i\hbar\partial_t\psi(\mathbf{r},t) = \Big(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r},t)\Big)\psi(\mathbf{r},t) \tag{2.42}$$

(energy is not conserved, but we still have $E = H$ classically and can 'quantize' this relation as before).

Note that a time-dependent potential usually corresponds to a classical description of an external field (e.g. the classical EM field), i.e. the time-dependent SE (2.42) usually describes a 'quantum particle' in a classical environment.

2.2.3 SE for a particle in the classical EM field

- step 1: derive classical Hamilton function

  (details can be found, e.g., in [Blöb] and [Kira], chap. 4.3.4)

  - Lorentz force
  $$\mathbf{F}_L = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \tag{2.43}$$
  - EM potentials are introduced via
  $$\begin{aligned} \mathbf{E} &= -\boldsymbol{\nabla}\phi - \partial_t\mathbf{A} && (2.44)\\ \mathbf{B} &= \boldsymbol{\nabla} \times \mathbf{A} && (2.45)\\ \hookrightarrow \quad \mathbf{F}_L &= q\Big(-\boldsymbol{\nabla}\phi - \partial_t\mathbf{A} + \big(\mathbf{v} \times (\boldsymbol{\nabla} \times \mathbf{A})\big)\Big) && (2.46) \end{aligned}$$
  - define 'generalized potential'
  $$W^* = q(\phi - \mathbf{A} \cdot \mathbf{v}) \tag{2.47}$$
  - show that
  $$\mathbf{F}_L = -\boldsymbol{\nabla}W^* + \frac{d}{dt}\frac{\partial}{\partial\mathbf{v}}W^* \tag{2.48}$$
  - Lagrangian
  $$L = T - W^* = \frac{1}{2}mv^2 - q\phi + q\mathbf{v} \cdot \mathbf{A} \tag{2.49}$$
  - Hamilton function
  $$H = \mathbf{p} \cdot \mathbf{v} - L = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi \tag{2.50}$$

    with canonical momentum
    $$\mathbf{p} = \frac{\partial L}{\partial\mathbf{v}} = m\mathbf{v} + q\mathbf{A} \tag{2.51}$$

– add another external potential V

$$\hookrightarrow \quad H = \frac{1}{2m}(\mathbf{p} - q\mathbf{A})^2 + q\phi + V \tag{2.52}$$

- step 2: quantization as usual

$$\mathbf{p} \longrightarrow \hat{\mathbf{p}} = \frac{\hbar}{i}\boldsymbol{\nabla}$$

$$\hookrightarrow \quad (\hat{E} - \hat{H})\psi = 0$$

$$\begin{aligned} i\hbar\partial_t\psi(\mathbf{r},t) &= \left(\frac{1}{2m}\Big(\frac{\hbar}{i}\boldsymbol{\nabla} - q\mathbf{A}(\mathbf{r},t)\Big)^2 + q\phi(\mathbf{r},t) + V(\mathbf{r})\right)\psi(\mathbf{r},t) \\ &= \left(-\frac{\hbar^2}{2m}\Delta + \frac{q^2}{2m}\mathbf{A}^2(\mathbf{r},t) + q\phi(\mathbf{r},t) + V(\mathbf{r})\right)\psi(\mathbf{r},t) \\ &\quad - \frac{\hbar q}{2mi}\left(\boldsymbol{\nabla}\cdot\Big(\mathbf{A}(\mathbf{r},t)\psi(\mathbf{r},t)\Big) + \mathbf{A}(\mathbf{r},t)\boldsymbol{\nabla}\psi(\mathbf{r},t)\right) \end{aligned}$$

in Coulomb gauge ([Jac], chap. 6.5) for source-free fields we have

$$\boldsymbol{\nabla}\cdot\mathbf{A} = 0\ , \quad \phi = 0$$

$$i\hbar\partial_t\psi(\mathbf{r},t) = \left\{-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r}) - \frac{q}{m}\frac{\hbar}{i}\mathbf{A}(\mathbf{r},t)\cdot\boldsymbol{\nabla} + \frac{q^2}{2m}\mathbf{A}^2(\mathbf{r},t)\right\}\psi(\mathbf{r},t) \tag{2.53}$$

comment: one step towards QED would be to 'quantize' in (2.53) the vector potential $\mathbf{A}$ (but we would need some additional rules to do that).

2.2.4 SE for N particles

- conservative classical system:

$$E = H(\mathbf{r}_1...\mathbf{r}_N, \mathbf{p}_1...\mathbf{p}_N) \tag{2.54}$$

- quantization:

$$\hat{H} = H(\mathbf{r}_1...\mathbf{r}_N, \hat{\mathbf{p}}_1...\hat{\mathbf{p}}_N) \tag{2.55}$$

with $\hat{\mathbf{p}}_i = \frac{\hbar}{i}\boldsymbol{\nabla}_i$

- SE

$$\hookrightarrow \quad i\hbar\partial_t\Psi = \hat{H}\Psi \tag{2.56}$$

$$\text{note that} \qquad \Psi = \Psi(\mathbf{r}_1...\mathbf{r}_N, t) \tag{2.57}$$

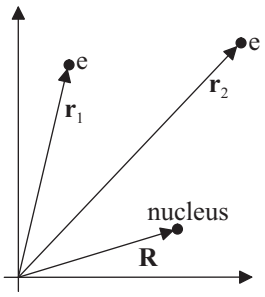
i.e. Ψ is defined on $3N$-dimensional configuration space!

- Example: Atom with $N = Z$ electrons

$$\hookrightarrow \quad i\hbar\partial_t \Psi(\mathbf{R}, \mathbf{r}_1 ... \mathbf{r}_N, t) =$$

$$= \left\{ -\hbar^2 \left(\frac{\Delta_R}{2M} + \sum_{i=1}^{N} \frac{\Delta_i}{2m} \right) - \sum_{i=1}^{N} \frac{Ze^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{R}|} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 |\mathbf{r}_i - \mathbf{r_j}|} \right\}$$

$$\times \Psi(\mathbf{R}, \mathbf{r}_1 ... \mathbf{r}_N, t) \tag{2.58}$$



$\rightarrow$ this eq. cannot be solved analytically for $N > 1$. It contains many aspects of the observable properties of atoms (atomic structure) and can be solved with good accuracy by 'numerical' or approximate methods.

2.3 Statistical interpretation

2.3.1 Problems with the concept of 'matter waves' and the solution

a) $\psi \in \mathbb{C} \quad \longrightarrow \quad$ not observable

can we interpret $\rho = |\psi|^2$ as a density
(such that $q\rho$ would be a 'classical' charge density)?

b) Spreading of wave packets (concerns also $\rho(\mathbf{r}, t)$!)

c) Self interaction of a charge density

according to classical electrodynamics $\rho(\mathbf{r}, t)$ should be the source of an electric field (Poisson eq.)! This was not taken into account in the Schrödinger eq.!

d) What does $|\Psi(\mathbf{r}_1 ... \mathbf{r}_N, t)|^2$ mean?

Obviously, it is not a charge density in ordinary space!

e) Double-slit experiment with electrons cannot be described in terms of classical waves only (neither in terms of classical particles)

$\longrightarrow$ this is best explained in [Fey], Vol III

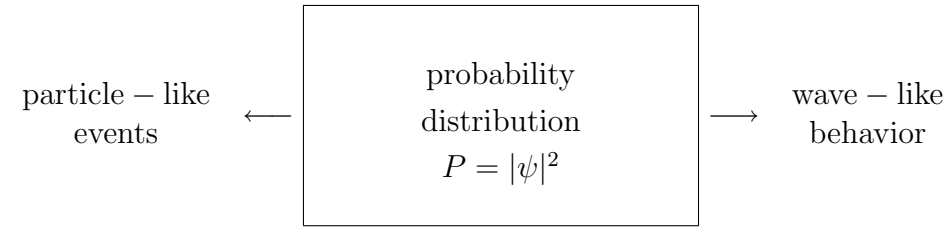
Solution: Born's statistical interpretation (1926)[1]:

$$\rho(\mathbf{r},t) \equiv |\psi(\mathbf{r},t)|^2 = \psi^*(\mathbf{r},t)\psi(\mathbf{r},t)$$

is a measure for the probability to find a particle at time t at position $\mathbf{r}$.

$\longrightarrow$ this is the link between the 'wave picture' and the 'particle picture' and allows a consistent description of experiments with quantum particles such as electrons or photons.

$\longrightarrow$ probability distribution $|\psi|^2$ is - for a given initial state $\psi_0 = \psi(t_0)$ - uniquely determined by the Schrödinger eq., but the behavior of a given particle is 'random' (i.e., it cannot be predicted).



2.3.2 Probabilities, norm, continuity

$\psi(\mathbf{r},t)$	:	probability amplitude
$\|\psi(\mathbf{r},t)\|^2$	:	probability density
$\|\psi(\mathbf{r},t)\|^2\ d^3r$	:	probability to find particle within d^3r

Normalization (for one particle)

$$N = \int_\infty |\psi(\mathbf{r},t)|^2\ d^3r = 1 \tag{2.59}$$

$\hookrightarrow$ conditions: a) ψ quadratically integrable (square-integrable) i.e. $N < \infty$
b) $N(t) = N = \text{const.}$

$\longrightarrow$ a) is fulfilled, e.g., for the GWP, but not for plane waves!

prove b) :
$$\frac{dN}{dt} = \int \partial_t |\psi(\mathbf{r},t)|^2\ d^3r = 0 \tag{2.60}$$

proof :

$$\begin{aligned} \partial_t|\psi(\mathbf{r},t)|^2 &= \psi^*\partial_t\psi + (\partial_t\psi^*)\psi \\ &\overset{\text{use SE}}{=} \frac{1}{i\hbar}\Big[\psi^*(\hat{H}\psi) - (\hat{H}\psi)^*\psi\Big] \\ \text{with}\qquad \hat{H} &= -\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\ , \qquad (V = V^*) \\ \hookrightarrow\quad \partial_t|\psi(\mathbf{r},t)|^2 &= \frac{i\hbar}{2m}\Big[\psi^*\Delta\psi - (\Delta\psi)^*\psi\Big] \end{aligned} \tag{2.61}$$

[1] In a footnote of an article about e^--atom scattering

use Green's theorem[2]

$$\hookrightarrow \quad \frac{dN}{dt} = \frac{i\hbar}{2m} \int_{S\to\infty} \left(\psi^* \frac{d\psi}{dn} - \frac{d\psi^*}{dn} \psi \right) df = 0$$

(because $\psi(\infty) = \frac{d\psi}{dn}(\infty) = 0$)(for well-behaved quadratically integrable functions)
(by the way: we have proven the hermiticity of $\hat{H}$ - see Section 3.1.2)

- differential form of norm conservation

  start from eq. (2.61):

$$\begin{aligned} \frac{i\hbar}{2m} \left[\psi^* \Delta\psi - (\Delta\psi)^* \psi \right] &= -\frac{i\hbar}{2m} \operatorname{div}(\psi \boldsymbol{\nabla} \psi^* - \psi^* \boldsymbol{\nabla} \psi) \\ &\equiv -\operatorname{div} \underbrace{\mathbf{j}(\mathbf{r}, t)}_{\text{'current density'}} \end{aligned}$$

$$\hookrightarrow \quad \partial_t \rho + \operatorname{div} \mathbf{j} = 0 \qquad \text{(continuity equation)} \tag{2.62}$$

  note that eq. (2.61) is also valid for non-square integrable functions, for which $N \longrightarrow \infty$.

  check it for a plane wave $\psi(\mathbf{r}, t) = e^{i(\mathbf{kr} - \omega t)}$

$$\begin{aligned} \rho(\mathbf{r}, t) &= 1 \,, \qquad \partial_t \rho = 0 \\ \mathbf{j}(\mathbf{r}, t) &= \frac{i\hbar}{2m} (\psi \boldsymbol{\nabla} \psi^* - \psi^* \boldsymbol{\nabla} \psi) = \frac{\hbar k}{m} \\ \operatorname{div} \mathbf{j} &= 0 \end{aligned}$$

2.3.3 Probability densities in coordinate and momentum space

Wave functions:

$$\psi(\mathbf{r}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int \phi(\mathbf{p}, t) e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} \, d^3 p \tag{2.63}$$

$$\phi(\mathbf{p}, t) = \frac{1}{(2\pi\hbar)^{\frac{3}{2}}} \int \psi(\mathbf{r}, t) e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{r}} \, d^3 r \tag{2.64}$$

---

[2] $$\int_V \left(\phi \Delta\psi - \psi \Delta\phi \right) d^3 r = \oint_{S(V)} \left(\phi \frac{\partial \psi}{\partial n} - \psi \frac{\partial \phi}{\partial n} \right) df$$

(cf. eqs. (2.12) - (2.14)): $\psi(\mathbf{r},t)$ and $\phi(\mathbf{p},t)$ are a Fourier transform pair.

Definition of probability densities:

$$\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 \tag{2.65}$$
$$P(\mathbf{p},t) = |\phi(\mathbf{p},t)|^2 \tag{2.66}$$

Note that for a free MWP we have $P(\mathbf{p},t) = P(\mathbf{p},0)$, but $\rho(\mathbf{r},t) \neq \rho(\mathbf{r},0)$, i.e. the wave packet spreads in position space, but not in momentum space. The stationarity of $P(\mathbf{p})$ reflects momentum conservation of a free particle!

We can prove that

$$N = 1 = \int \rho(\mathbf{r},t)\ d^3r = \int P(\mathbf{p},t)\ d^3p \tag{2.67}$$

proof:

$$\begin{aligned}
\lhd \qquad \int \psi_1^*(\mathbf{r})\psi_2(\mathbf{r})\ d^3r &= \frac{1}{(2\pi\hbar)^3}\int d^3r \int d^3p \int d^3p' e^{-\frac{i}{\hbar}(\mathbf{p}-\mathbf{p}')\mathbf{r}}\ \phi_1^*(\mathbf{p}')\phi_2(\mathbf{p}) \\
&= \frac{1}{(2\pi\hbar)^3}\int d^3p \int d^3p' \Big(\phi_1^*(\mathbf{p}')\phi_2(\mathbf{p}) \int e^{-\frac{i}{\hbar}(\mathbf{p}-\mathbf{p}')\mathbf{r}}\ d^3r\Big) \\
&= \int d^3p \int d^3p'\ \phi_1^*(\mathbf{p}')\phi_2(\mathbf{p})\delta(\mathbf{p}'-\mathbf{p}) \\
&= \int \phi_1^*(\mathbf{p})\phi_2(\mathbf{p})\ d^3p \\
&\quad \text{(this is Parseval's relation)}
\end{aligned}$$

(eq. (2.67) follows for $\psi_1 = \psi_2$)

Since Fourier transformation is a unique, invertible mapping, position and momentum wave functions are completely equivalent (i.e. they carry the same information)

2.3.4 Expectation values

$\longrightarrow$ probability interpretation of QM implies that notions of probability theory, such as the expectation value of a distribution can be defined

- In one dimension (classically + QM)

  $\left.\begin{array}{l} \langle x\rangle = \int x\rho(x)\ dx \\ \\ \int \rho(x)\ dx = 1 \end{array}\right\}$ valid for a continuous classical distribution

  QM ingredient: $\rho(x) = |\psi(x)|^2$

- In three dimensions

$$\langle x\rangle(t) = \int x\rho(\mathbf{r},t)\ d^3r \tag{2.68}$$

(if $\partial_t\rho \neq 0 \quad\longrightarrow\quad \langle x\rangle(t) \ = \ \langle x\rangle(t_0)$)

write

$$\langle x\rangle(t) \ = \ \int \psi^*(\mathbf{r},t)x\psi(\mathbf{r},t)\ d^3r \tag{2.69}$$

$$\langle \mathbf{r}\rangle(t) \ = \ \int \psi^*(\mathbf{r},t)\mathbf{r}\psi(\mathbf{r},t)\ d^3r \tag{2.70}$$

in general

$$\langle F(\mathbf{r},t)\rangle = \int \psi^*(\mathbf{r},t)F(\mathbf{r},t)\psi(\mathbf{r},t)\ d^3r \tag{2.71}$$

- momentum space
$\longrightarrow$ apply the same rule:

$$\langle \mathbf{p}\rangle(t) \ = \ \int \mathbf{p}P(\mathbf{p},t)\ d^3p \ = \ \int \phi^*(\mathbf{p},t)\mathbf{p}\phi(\mathbf{p},t)\ d^3p \tag{2.72}$$

$$\langle G(\mathbf{p},t)\rangle \ = \ \int \phi^*(\mathbf{p},t)G(\mathbf{p},t)\phi(\mathbf{p},t)\ d^3p \tag{2.73}$$

Example:

$$E \ \equiv \ \langle H\rangle \ = \ \langle T\rangle + \langle V\rangle$$

$$= \int \phi^*(\mathbf{p},t)\frac{\mathbf{p}^2}{2m}\phi(\mathbf{p},t)\ d^3p + \int \psi^*(\mathbf{r},t)V(\mathbf{r})\psi(\mathbf{r},t)\ d^3r \tag{2.74}$$

can we express $\langle H\rangle$ as an integral over d^3r only (or over d^3p only)?

$$\text{consider :} \qquad \partial_x\psi(\mathbf{r},t) \ = \ \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int \phi(\mathbf{p},t)\partial_x e^{\frac{i}{\hbar}\mathbf{pr}}\ d^3p$$

$$= \ \frac{1}{(2\pi\hbar)^{\frac{3}{2}}}\int \phi(\mathbf{p},t)\frac{i}{\hbar}p_x e^{\frac{i}{\hbar}\mathbf{pr}}\ d^3p$$

i.e. we have a Fourier transform pair $\frac{\hbar}{i}\partial_x\psi \ \longleftrightarrow \ p_x\phi$

$$\hookrightarrow \quad \langle p_x\rangle(t) \quad = \quad \int \phi^*(\mathbf{p},t)p_x\phi(\mathbf{p},t)\ d^3p$$

$$\overset{\text{Parseval}}{=} \quad \int \psi^*(\mathbf{r},t)\frac{\hbar}{i}\partial_x\psi(\mathbf{r},t)\ d^3r$$

$$= \quad \int \psi^*(\mathbf{r},t)\hat{p}_x\psi(\mathbf{r},t)\ d^3r \tag{2.75}$$

With the same argument we obtain

$$\langle \mathbf{p} \rangle(t) = \int \psi^*(\mathbf{r},t)\hat{\mathbf{p}}\psi(\mathbf{r},t)\ d^3r \qquad (\text{with } \hat{\mathbf{p}} = \frac{\hbar}{i}\nabla) \tag{2.76}$$

and in general

$$\begin{aligned} \langle G(\mathbf{p},t) \rangle &= \int \psi^*(\mathbf{r},t) G\Big(\frac{\hbar}{i}\nabla, t\Big)\psi(\mathbf{r},t)\ d^3r \qquad (2.77) \\ \text{e.g.} \qquad \langle T \rangle &= -\frac{\hbar^2}{2m}\int \psi^*(\mathbf{r},t)\Delta\psi(\mathbf{r},t)\ d^3r \end{aligned}$$

Remarks:

- These relations justify the definition of the sign in $\hat{\mathbf{p}}$ (cf. page 14)
- The average momentum is related to the current density (for quadratically integrable wave functions):

$$\langle \mathbf{p} \rangle(t) = m \int \mathbf{j}(\mathbf{r},t)\ d^3r$$

We can apply a similar argument to show that

$$\begin{aligned} \langle \mathbf{r} \rangle &= \int \phi^*(\mathbf{p},t) i\hbar \boldsymbol{\nabla}_p \phi(\mathbf{p},t)\ d^3p \qquad (2.78) \\ \text{and} \qquad \langle F(\mathbf{r},t) \rangle &= \int \phi^*(\mathbf{p},t) F(i\hbar\boldsymbol{\nabla}_p, t)\phi(\mathbf{p},t)\ d^3p \qquad (2.79) \end{aligned}$$

Note that expressions $F(i\hbar\boldsymbol{\nabla}_p, t)$, $G(\frac{\hbar}{i}\boldsymbol{\nabla}, t)$ do not work in all cases, e.g. for the Coulomb potential $|\mathbf{r}|$ appears in the denominator!

Examples:

(i) One-dimensional harmonic oscillator
classical Hamilton function:

$$H(x, p_x) = \frac{p_x^2}{2m} + \frac{m}{2}\omega_0^2 x^2$$

$$\begin{aligned} \hookrightarrow \quad \langle E \rangle(t) &= \langle H \rangle(t) \\ &= \int \psi^*(x,t)\Big(-\frac{\hbar^2}{2m}\partial_x^2 + \frac{m}{2}\omega_0^2 x^2\Big)\psi(x,t)\ dx \\ &= \int \phi^*(p_x,t)\Big(\frac{p_x^2}{2m} - \frac{m}{2}\hbar^2\omega_0^2\partial_{p_x}^2\Big)\phi(p_x,t)\ dp_x \end{aligned}$$

(ii) Free particle

We can write for the position expectation value:

$$\langle \mathbf{r} \rangle(t) = \int \phi^*(\mathbf{p},t) i\hbar \boldsymbol{\nabla}_p \phi(\mathbf{p},t)\ d^3p$$

with $\phi(\mathbf{p},t) = \phi(\mathbf{p},0) e^{-\frac{i}{\hbar}\frac{\mathbf{p}^2}{2m}t}$

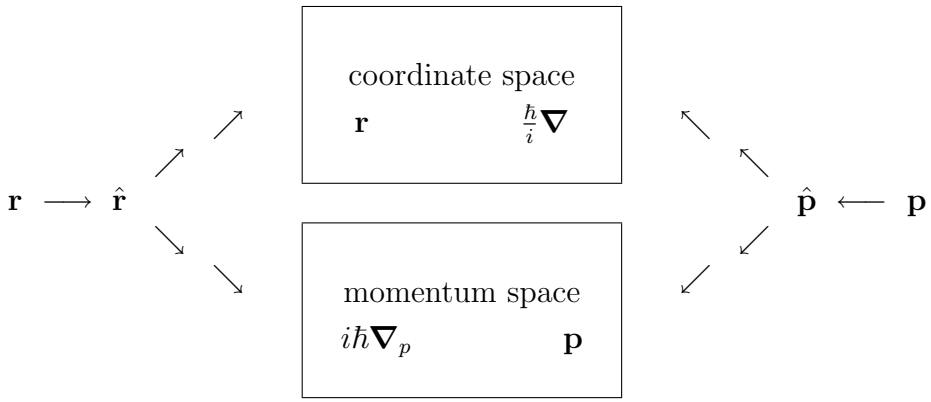
$$\begin{aligned}
\hookrightarrow \quad \langle \mathbf{r} \rangle(t) &= \int \phi^*(\mathbf{p},0) e^{\frac{i}{\hbar}\frac{\mathbf{p}^2}{2m}t} i\hbar \boldsymbol{\nabla}_p \Big(\phi(\mathbf{p},0) e^{-\frac{i}{\hbar}\frac{\mathbf{p}^2}{2m}t} \Big)\ d^3p \\
&= \int \phi^*(\mathbf{p},0) e^{\frac{i}{\hbar}\frac{\mathbf{p}^2}{2m}t} \Big\{ i\hbar \boldsymbol{\nabla}_p \phi(\mathbf{p},0) + \frac{\mathbf{p}}{m} t\, \phi(\mathbf{p},0) \Big\} e^{-\frac{i}{\hbar}\frac{\mathbf{p}^2}{2m}t}\ d^3p \\
&= \int \phi^*(\mathbf{p},0) i\hbar \boldsymbol{\nabla}_p \phi(\mathbf{p},0)\ d^3p + \frac{t}{m} \int \phi^*(\mathbf{p},0) \mathbf{p} \phi(\mathbf{p},0)\ d^3p \\
&= \langle \mathbf{r} \rangle(t=0) + \frac{\langle \mathbf{p} \rangle}{m} t
\end{aligned}$$

$$\hookrightarrow \qquad \frac{d}{dt}\langle \mathbf{r} \rangle = \frac{\langle \mathbf{p} \rangle}{m} = \frac{\hbar \mathbf{k}_0}{m} = \mathbf{v}_{gr}$$

This is a special case of Ehrenfest's theorems (see exercises and Section 3.4.2)

We have seen that we can evaluate expectation values either in coordinate space or in momentum space. Both 'representations' are fully equivalent (below we will see that we can even rewrite the SE as an equation for $\phi(\mathbf{p},t)$)

Note the extended correspondence rule (cf eqs. (2.33) - (2.35))



2.4 Solution of the Schrödinger equation → quantum effects

2.4.1 Stationary (time-independent) SE

Consider eqs. (2.40), (2.41); i.e., SE for a time-independent potential $V(\mathbf{r})$. Note that $i\hbar\partial_t\psi(\mathbf{r},t) = \hat{H}\psi(\mathbf{r},t)$ is an initial-value problem (i.e. solution is unique for a given initial state $\psi(\mathbf{r},t_0) = \psi_0(\mathbf{r})$)

- Ansatz
$$\psi(\mathbf{r},t) = \psi(\mathbf{r})f(t) \tag{2.80}$$
→ insertion into SE eq. (2.40)
$$\hookrightarrow \quad \frac{i\hbar\dot{f}(t)}{f(t)} = \frac{\hat{H}\psi(\mathbf{r})}{\psi(\mathbf{r})} = \text{const.} \equiv A \tag{2.81}$$
↪ separate eqs.:
$$\dot{f} = -\frac{i}{\hbar}Af\ , \quad \hookrightarrow f(t) = e^{-\frac{i}{\hbar}At} \tag{2.82}$$
$$\hat{H}\psi(\mathbf{r}) = A\psi(\mathbf{r}) \tag{2.83}$$

- What is A?
$$\begin{aligned} \lhd \qquad E = \langle\hat{H}\rangle &= \int \psi^*(\mathbf{r},t)\hat{H}\psi(\mathbf{r},t)\ d^3r = \int \psi^*(\mathbf{r})\hat{H}\psi(\mathbf{r})\ d^3r \\ &= \int \psi^*(\mathbf{r})A\psi(\mathbf{r})\ d^3r = A\int \psi^*(\mathbf{r})\psi(\mathbf{r})\ d^3r \\ &= A \end{aligned}$$
↪ solution of SE (eq. (2.40)) has the form
$$\psi_E(\mathbf{r},t) = \psi_E(\mathbf{r})e^{-\frac{i}{\hbar}Et} \tag{2.84}$$
and describes a state with constant energy.

Properties:

- $\rho(\mathbf{r},t) = |\psi_E(\mathbf{r},t)|^2 = |\psi_E(\mathbf{r})|^2 = \rho(\mathbf{r})$
- $\partial_t\rho = 0 \quad \Longrightarrow \quad \text{div}\ \mathbf{j} = 0 \quad (\text{and } \mathbf{j} = \mathbf{j}(\mathbf{r}))$
- $\frac{d}{dt}\langle\hat{A}\rangle = 0$ for all operators $\frac{\partial\hat{A}}{\partial t} = 0$

⟶ the states (2.84) are called stationary states

The task then is to solve the stationary SE
$$\hat{H}\psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}) \tag{2.85}$$
which is an eigenvalue problem (see later), and which is specified completely only if boundary (and regularity) conditions are imposed.

- 'Weak' boundary conditions (always imposed)

  $\hookrightarrow$ $\psi_E(\mathbf{r}), \boldsymbol{\nabla}\psi_E(\mathbf{r})$ are continuous, unique, $< \infty$ (bounded)
  (they have implicitly been used in chapter [2.3] in order to deal with 'well-defined' probability and current densities)

- In general, one can distinguish two types of solutions of (2.85):

  a) bound states
  a classical bound particle cannot escape to infinity
  $\longrightarrow$ the quantum particle must fulfill $\psi_E(\mathbf{r}) \overset{r\to\infty}{\longrightarrow} 0$

  $$\Longrightarrow \quad \int_\infty |\psi_E(\mathbf{r})|^2 \, d^3r < \infty$$

  $\longrightarrow$ this 'strong' boundary condition leads to quantized states and a discrete spectrum (i.e. only a discrete subset of energies E is allowed in eq. (2.85))

  b) scattering states
  classically, a scattered particle may escape to infinity
  $\longrightarrow$ $\psi_E(\mathbf{r}) \overset{r\to\infty}{\longrightarrow}$ finite value

  $$\longrightarrow \quad \int_\infty |\psi_E(\mathbf{r})|^2 \, d^3r \longrightarrow \infty$$

  $\longrightarrow$ continuous spectrum (all energies E are possible)

- Extract strategy for the solution of time-dependent SE for time-independent potentials:

  1. Solve stationary SE $\longrightarrow$ obtain $E, \psi_E(\mathbf{r})$
  2. A reasonably well-behaved initial-state $\psi_0(\mathbf{r})$ can be represented by a linear combination of stationary states
  3. Apply principle of superposition: the corresponding linear combination of stationary states describes solution of time-dependent SE for all times

  For bound state problems one usually deals only with the first issue.

2.4.2 One-dimensional model systems

Stationary SE takes the form

$$\psi''(x) + (\varepsilon - U(x))\psi(x) = 0 \tag{2.86}$$

$$\varepsilon = \frac{2m}{\hbar^2}E \ , \quad U = \frac{2m}{\hbar^2}V$$

Eq. (2.86) is an ordinary differential equation of second order and of Sturm-Liouville type.

$\longrightarrow$ general solution:

$$\psi = \psi_\varepsilon(x) = \alpha_1\psi_1^\varepsilon(x) + \alpha_2\psi_2^\varepsilon(x)$$

eigenvalue ε is two-fold degenerate

a) The free particle (again)

Step 1:

Solutions of eq. (2.86) for $U = 0$ and $\varepsilon \geq 0$:

$$\begin{aligned} \psi_\varepsilon(x) &= Ae^{ikx} + Be^{-ikx} \\ k &= \sqrt{\varepsilon} \end{aligned}$$

$\hookrightarrow$ stationary states (cf. eq. (2.84))

$$\begin{aligned} \psi_\varepsilon(x,t) &= Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)} \\ \omega &= \frac{\hbar k^2}{2m} \end{aligned}$$

$$\int_{-\infty}^{\infty} |\psi_\varepsilon(x,t)|^2 \, dx = \int_{-\infty}^{\infty} |\psi_\varepsilon(x)|^2 \, dx \quad \longrightarrow \quad \infty$$

$\longrightarrow$ continuous spectrum (weak boundary conditions only)

Step 2: Represent initial-state wavepacket ($t_0 = 0$)

$$\begin{aligned} \psi_0(x) &= \int_0^\infty \left(A(k)e^{ikx} + B(k)e^{-ikx} \right) dk \\ &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{A}(k)e^{ikx} \, dk \qquad \text{(cf. eq. (2.15))} \end{aligned}$$

Typically, $\psi_0(\mathbf{r})$ is given explicitly (e.g. as a GWP), and the task is to determine $\tilde{A}(k)$ (by inverse FT)

Step 3: Apply principle of superposition

$$\hookrightarrow \quad \psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{A}(k)e^{i(kx-\omega t)} \, dk$$

Remarks:

(i) WPs solve time-dependent SE

(ii) On the other hand PWs are eigenfunctions of $\hat{H}$, but not appropriate wave functions for particles (well: not really...)

(iii) Think of PW as (non-normalized) limit of WP with width $\Delta k \to 0$

(iv) $\boxed{\varepsilon < 0 :}$

$$\begin{aligned} \psi_\varepsilon(x) &= Ae^{\kappa x} + Be^{-\kappa x} \\ \kappa &= \sqrt{-\varepsilon} \end{aligned} \tag{2.87}$$

boundary conditions: $\psi_\varepsilon(x) < \infty \quad \forall\, x$

$$\begin{aligned} \Longrightarrow \quad & x \longrightarrow -\infty \quad \hookrightarrow \quad B = 0 \\ & x \longrightarrow +\infty \quad \hookrightarrow \quad A = 0 \\ \hookrightarrow \quad & \psi_\varepsilon(x) = 0 \end{aligned}$$

(free particle with $\varepsilon < 0$ does not exist (in nonrelativistic QM))

b) General remarks about piecewise constant potentials

We will consider potentials of the type $U(x) = U_i$ for $x \in [a_i, b_i]$;

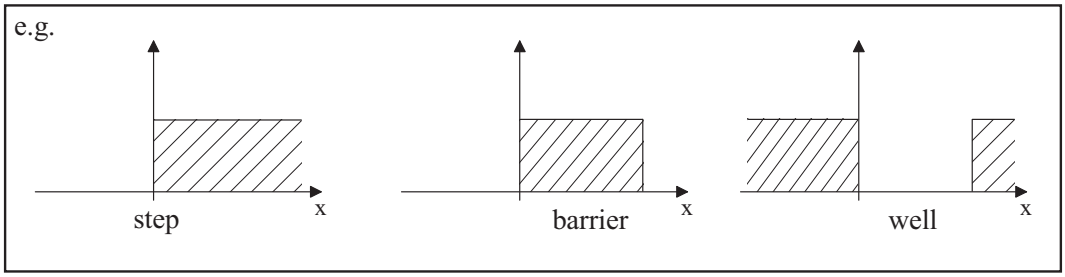


Figure 2.4: Different types of piecewise constant potentials

Scheme:

1) Solve SE (2.86) in all intervals, in which U is constant, separately

- $\varepsilon > U_i$

$$\begin{aligned} k_i &= \sqrt{\varepsilon - U_i} > 0 \\ \text{SE}: \quad & \psi''(x) + k_i^2 \psi(x) = 0 \\ \text{solution}: \quad & \psi_\varepsilon(x) = Ae^{ik_i x} + Be^{-ik_i x} \\ & = \tilde{A} \sin(k_i x + \varphi) \end{aligned} \tag{2.88}$$

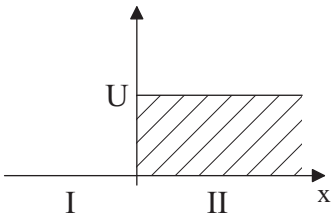
- $\varepsilon < U_i$

$$\begin{aligned} \hookrightarrow \quad k_i &= \sqrt{\varepsilon - U_i} = i\sqrt{U_i - \varepsilon} \\ \kappa_i &:= -ik_i = \sqrt{U_i - \varepsilon} > 0 \end{aligned}$$

$$\begin{aligned} \text{SE}: \qquad & \psi''(x) - \kappa_i^2 \psi(x) = 0 \\ \text{solution}: \qquad & \psi_\varepsilon(x) = Ae^{\kappa_i x} + Be^{-\kappa_i x} \end{aligned} \tag{2.89}$$

2) Matching and boundary conditions
$\longrightarrow$ for n intervals with constant potentials $U_i ... U_n$ we have $(2n-2)$ matching conditions
$\longrightarrow$ 2 constants remain (fixed by normalization and phase $\rightarrow$ initial condition of physical problem)

c) Potential step



$$U(x) = U\theta(x) \equiv \begin{cases} 0 & x < 0 \\ U & x \geq 0 \end{cases}$$

$$\psi_\varepsilon(x) = \theta(-x)\psi_I(x) + \theta(x)\psi_{II}(x) \tag{2.90}$$

1) $\boxed{\varepsilon > U}$:

$$\psi_I(x) = Ae^{ik_I x} + Be^{-ik_I x} \tag{2.91}$$
$$\psi_{II}(x) = Ce^{ik_{II} x} + De^{-ik_{II} x} \tag{2.92}$$
$$k_I = \sqrt{\varepsilon} \tag{2.93}$$
$$k_{II} = \sqrt{\varepsilon - U} = \sqrt{k_I^2 - U} \tag{2.94}$$

matching conditions:

$$\psi_I(0) = \psi_{II}(0) \tag{2.95}$$
$$\psi_I'(0) = \psi_{II}'(0) \tag{2.96}$$

choose $A = 1$, $D = 0$ (justification follows)

eqs. (2.95) + (2.96) yield $\left| \begin{array}{c} 1 + B = C \\ \\ ik_I - ik_I B = ik_{II} C \end{array} \right|$

$$B = \frac{k_I - k_{II}}{k_I + k_{II}} \ , \quad C = \frac{2k_I}{k_I + k_{II}} \tag{2.97}$$

$$\begin{aligned}
\psi_\varepsilon(x,t) &= \Big\{\psi_{in}(x)\theta(-x) + \psi_{ref}(x)\theta(-x) + \psi_{trans}(x)\theta(x)\Big\}e^{-i\omega t} \\
\psi_{in}(x) &= e^{ik_I x} \\
j_{in}(x) &= \frac{i\hbar}{2m}\big(\psi_{in} d_x\psi^*_{in} - \psi^*_{in} d_x\psi_{in}\big) = \frac{\hbar k_I}{m}
\end{aligned} \tag{2.98}$$

(cf. eq. (2.62))

$$\begin{aligned}
\psi_{ref}(x) &= \frac{k_I - k_{II}}{k_I + k_{II}} e^{-ik_I x} \\
j_{ref}(x) &= -\Big(\frac{k_I - k_{II}}{k_I + k_{II}}\Big)^2 \frac{\hbar k_I}{m}
\end{aligned} \tag{2.99}$$

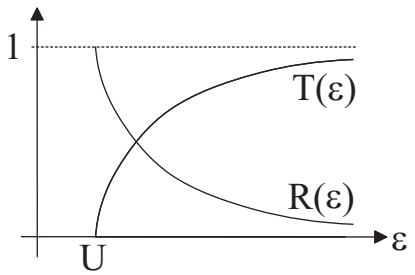
$$\begin{aligned}
\psi_{trans}(x) &= \frac{2k_I}{k_I + k_{II}} e^{ik_{II} x} \\
j_{trans}(x) &= \Big(\frac{2k_I}{k_I + k_{II}}\Big)^2 \frac{\hbar k_{II}}{m}
\end{aligned} \tag{2.100}$$

define reflection coefficient R and transmission coefficient T

$$R = \left|\frac{j_{ref}}{j_{in}}\right| = \left(\frac{k_I - k_{II}}{k_I + k_{II}}\right)^2 \tag{2.101}$$

$$T = \left|\frac{j_{trans}}{j_{in}}\right| = \frac{4k_I k_{II}}{(k_I + k_{II})^2} \tag{2.102}$$

$$\Longrightarrow \quad R + T = 1$$



(if we choose $A = 0, D = 1$, we obtain the same R, T)

Note that R, T have to be interpreted as probabilities for reflection and transmission. The individual event (as stated on page 17) is not determined. Each particle is either reflected or transmitted; i.e. the wave packet splits, but not the particle!

consider WPs for further analysis

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(k_I)\psi_\varepsilon(x) e^{-i\omega t}\, dk_I \tag{2.103}$$

solves time-dependent SE if ψ_ε solves stationary SE. More explicitly:

$$\begin{aligned}\psi(x,t) &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(k_I)\Big\{\theta(-x)\Big[Ae^{i(k_I x-\omega t)}+Be^{-i(k_I x+\omega t)}\Big] \\ &+ \theta(x)\Big[Ce^{i(k_{II}x-\omega t)}+De^{-i(k_{II}x+\omega t)}\Big]\Big\}\, dk_I \qquad (2.104)\end{aligned}$$

note: $\omega = \omega(k_I) = \frac{\hbar k_I^2}{2m}$; $\quad k_{II} = k_{II}(k_I)$ $\quad$ (eq. (2.94))

Consider the motion of centers of WP (cf. eq. (2.22), (2.23)):

A) $\varphi_A(k_I) = k_I x - \omega t$

$$\left.\frac{d\varphi_A}{dk_I}\right|_{k_I^0} = 0 \quad \Longleftrightarrow \quad x_0^A = \frac{\hbar k_I^0}{m}t$$

$\longrightarrow$ moves to the right in I for $t < 0$ ($\rightarrow$ incoming WP)

B) $\varphi_B(k_I) = -k_I x - \omega t$

$$\hookrightarrow \quad x_0^B = -\frac{\hbar k_I^0}{m}t$$

$\longrightarrow$ moves to the left in I for $t > 0$ ($\rightarrow$ reflected WP)

C) $\varphi_C(k_I) = k_{II}(k_I)x - \omega(k_I)t$

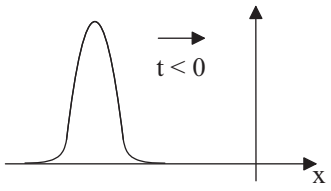
$$\hookrightarrow \quad x_0^C = \frac{\hbar k_{II}^0}{m}t$$

$\longrightarrow$ moves to the right in II for $t > 0$ ($\rightarrow$ transmitted WP)

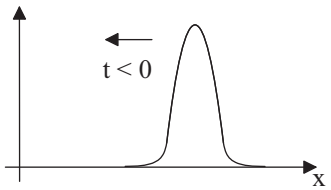
D) $\varphi_D(k_I) = -k_{II}(k_I)x - \omega(k_I)t$

$$\hookrightarrow \quad x_0^D = -\frac{\hbar k_{II}^0}{m}t$$

$\longrightarrow$ moves to the left in II for $t < 0$



If we choose $A = 1, D = 0$, we choose the initial condition corresponding to an incoming WP from left to right



If we choose $A = 0, D = 1$, the incoming WP moves from the right to the left

$\longrightarrow$ due to eq. (2.104) we can speak of a splitting of the wave packet at $t \geq 0$; it is partly reflected and partly transmitted.

2) $\boxed{\varepsilon < U}$:

$$\begin{aligned} \psi_I(x) &= Ae^{ikx} + Be^{-ikx} && (2.105)\\ \psi_{II}(x) &= Ce^{\kappa x} + De^{-\kappa x} && (2.106)\\ k \equiv k_I &= \sqrt{\varepsilon}\ , \quad \kappa = \sqrt{U-\varepsilon}\ > 0 && (2.107) \end{aligned}$$

- $\psi(x) < \infty \quad \forall\ x \qquad \hookrightarrow \quad C = 0$

$$\hookrightarrow \quad \psi_\varepsilon(x) = \theta(-x)\Big\{Ae^{ikx} + Be^{-ikx}\Big\} + \theta(x)De^{-\kappa x} \qquad (2.108)$$

- choose $A = 1$
- matching conditions (2.95) + (2.96) yield

$$B = -\frac{\kappa + ik}{\kappa - i\kappa}\ , \quad D = -\frac{2ik}{\kappa - ik} \qquad (2.109)$$

- current densities (cf. page 25)

$$\left.\begin{array}{l} j_{in} = \frac{\hbar k}{m} \\ j_{ref} = -j_{in} \\ j_{trans} = 0 \end{array}\right\} \Longrightarrow \quad T = 0\ , \quad R = 1 \qquad (2.110)$$

$\longrightarrow$ no current in classically forbidden region II, but finite probability density

$$\rho_{II}(x) = |\psi_{II}(x)|^2 = |D|^2 e^{-2Kx} = \frac{4k^2}{k^2+\kappa^2} e^{-2\kappa x} \qquad (2.111)$$

- define average 'penetration depth' x_m:

$$\rho_{II}(x_m) = \frac{1}{2}\rho_{II}(0) \quad \overset{(2.111)}{\Longrightarrow} \quad x_m = \frac{\ln 2}{2\kappa} \qquad (2.112)$$

- We can anticipate the tunnel effect: if the potential step has a finite width, i.e. becomes a barrier, there is a chance (i.e., a finite probability) to find the particle that comes from one side on the other side of the barrier (a quantum particle can penetrate a finite barrier)
- For our problem we have total reflection ($R = 1$), but as the particle can enter region II the reflection is (slightly) delayed

- WPs

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int f(k) \Big\{ \theta(-x) \Big[e^{i(kx-\omega t)} + B(k) e^{-i(kx+\omega t)} \Big] + \theta(x) D(k) e^{-\kappa x} e^{-i\omega t} \Big\} \, dk \tag{2.113}$$

note that $B(k) \overset{(2.109)}{=} |B(k)| e^{i\beta(k)} = e^{i\beta(k)}$

$$D(k) = |D(k)| e^{i\delta(k)} = \frac{2k}{\sqrt{\kappa^2 + k^2}} e^{i\delta(k)}$$

$\longrightarrow$ i.e. additional phases β, δ!

motion of center of WPs:

$\boxed{\psi_{in}}$ $x_0 = \frac{\hbar k_0}{m} t$ (as before)

$\boxed{\psi_{ref}}$ $\varphi(k) = -kx - \omega t + \beta(k)$

$$\hookrightarrow \quad x_0 = -\frac{\hbar k_0}{m} t + \left. \frac{d\beta}{dk} \right|_{k_0} \tag{2.114}$$

delay time:

$$\tau(x_0 = 0) = \frac{m}{\hbar k_0} \left. \frac{d\beta}{dk} \right|_{k_0} = \hbar \left. \frac{d\beta}{dE} \right|_{E_0} \tag{2.115}$$

$$\beta = \arctan \frac{\Im \, B}{\Re \, B} = \arctan \frac{2\sqrt{U\varepsilon - \varepsilon^2}}{U - 2\varepsilon} \tag{2.116}$$

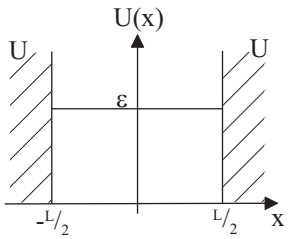
$$\frac{d\beta}{dE} = \frac{2m}{\hbar^2} \frac{d\beta}{d\varepsilon} = \frac{2m}{\hbar^2} \Big[\varepsilon(U-\varepsilon) \Big]^{-\frac{1}{2}} > 0 \, , \qquad (\text{for } \varepsilon \in]0, U[\,) \tag{2.117}$$

consider limit $U \longrightarrow \infty$

$\hookrightarrow \quad \kappa = \sqrt{U - \varepsilon} \approx \sqrt{U} \longrightarrow \infty \quad \hookrightarrow \quad \psi_{II}(x) = 0 \, , \quad (x > 0)$

wave function vanishes in regions where $U \longrightarrow \infty$

d) Infinitely deep potential well



$$U(x) = \begin{cases} 0 & -\frac{L}{2} \le x \le \frac{L}{2} \\ \infty & \text{else} \end{cases}$$

$$\psi_\varepsilon(x) = A e^{ikx} + B e^{-ikx} \, ; \quad k = \sqrt{\varepsilon} > 0 \tag{2.118}$$

- boundary conditions (see above)

$$\psi\Big(-\frac{L}{2}\Big) = \psi\Big(\frac{L}{2}\Big) = 0 \tag{2.119}$$

$$\longrightarrow \quad \left| \begin{array}{l} Ae^{-ik\frac{L}{2}} + Be^{ik\frac{L}{2}} = 0 \\ \\ Ae^{ik\frac{L}{2}} + Be^{-ik\frac{L}{2}} = 0 \end{array} \right|$$

$$\longrightarrow \quad \sin kL = 0 \quad \Longleftrightarrow \quad k = k_n = \frac{n\pi}{L} \tag{2.120}$$

$$\longrightarrow \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{1}{2m}\Big(\frac{\hbar\pi}{L}\Big)^2 n^2 \tag{2.121}$$

$\longrightarrow$ quantized energy levels!

- eigenfunctions:

$$\psi_n(x) = A\Big\{e^{ik_n x} - (-1)^n e^{-ik_n x}\Big\}\Big[\theta\Big(x+\frac{L}{2}\Big) - \theta\Big(x-\frac{L}{2}\Big)\Big] \tag{2.122}$$

- norm alization:

$$\begin{aligned} N &= 1 = \int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = \int_{-\frac{L}{2}}^{\frac{L}{2}} |\psi_n(x)|^2 \, dx \\ \Longrightarrow \quad A &= \frac{1}{\sqrt{2L}} \end{aligned}$$

$$\hookrightarrow \quad \psi_n(x) = \Big[\theta\Big(x+\frac{L}{2}\Big) - \theta\Big(x-\frac{L}{2}\Big)\Big]\sqrt{\frac{2}{L}} \begin{cases} \cos\frac{n\pi}{L}x \, , & n = 1,3,5,... \\ \\ i\sin\frac{n\pi}{L}x \, , & n = 2,4,... \end{cases}$$

(note that $\psi_0(x) \sim \sin 0x = 0$)

<u>discussion:</u>

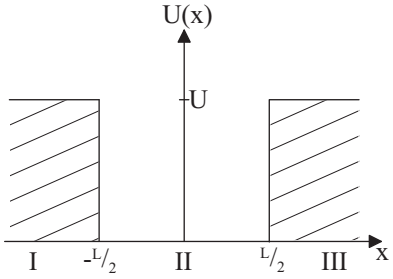
- Quantization $\hat{=}$ standing waves: de Broglie wavelength $\lambda_n^B = \frac{2\pi}{k_n} = \frac{2L}{n}$ is adapted to width of the well
- ground-state energy $E_1 = \frac{1}{2m}\Big(\frac{\hbar\pi}{L}\Big)^2 > 0$
  ($\longrightarrow$ zero point motion: bound particle cannot be at rest)
  Later on we will see that this is a consequence of the uncertainty relation
- quantization of energies $E_n \propto \frac{1}{m}$ $\longrightarrow$ level spacings become very small for heavy particles
- $\psi_n(x)$ has $n-1$ nodes (general result)

- parity; defined by

$$\psi(x) = \psi(-x) \qquad \text{even parity} \quad \text{(e.g. cosine)} \tag{2.123}$$
$$\psi(x) = -\psi(-x) \qquad \text{odd parity} \quad \text{(e.g. sine)} \tag{2.124}$$

in our case $U(x) = U(-x) \hookrightarrow$ eigenfunctions ψ_n have well-defined parity (see chapter (3.5.5))

e) Finite potential well



$$U(x) = \begin{cases} U & x < -\frac{L}{2} \\ 0 & -\frac{L}{2} \le x \le \frac{L}{2} \\ U & x > \frac{L}{2} \end{cases}$$

1) $\boxed{\varepsilon < U}$:

$$\psi_I(x) = Ae^{\kappa x} + Be^{-\kappa x} \tag{2.125}$$
$$\psi_{II}(x) = C\sin(kx + \varphi) \tag{2.126}$$
$$\psi_{III}(x) = De^{-\kappa x} + Ee^{\kappa x} \tag{2.127}$$
$$\kappa = \sqrt{U - \varepsilon} > 0\,, \quad k = \sqrt{\varepsilon} > 0 \tag{2.128}$$

- boundary condition: $\psi(x) < \infty \quad \forall\, x$

$$\hookrightarrow \quad B = E = 0$$

- matching conditions: consider

$$\psi_I\Big(-\frac{L}{2}\Big) = \psi_{II}\Big(-\frac{L}{2}\Big) \tag{2.129}$$
$$\psi_{II}\Big(\frac{L}{2}\Big) = \psi_{III}\Big(\frac{L}{2}\Big) \tag{2.130}$$

and logarithmic derivative $\frac{d}{dx}\ln\psi(x) = \frac{\psi'(x)}{\psi(x)}$ instead of derivative

$$\frac{\psi_I'(-\frac{L}{2})}{\psi_I(-\frac{L}{2})} = \frac{\psi_{II}'(-\frac{L}{2})}{\psi_{II}(-\frac{L}{2})} \tag{2.131}$$
$$\frac{\psi_{II}'(\frac{L}{2})}{\psi_{II}(\frac{L}{2})} = \frac{\psi_{III}'(\frac{L}{2})}{\psi_{III}(\frac{L}{2})} \tag{2.132}$$

From eqs. (2.131) + (2.132) we get

$$\longrightarrow \quad \left| \begin{array}{c} \frac{k}{\kappa} = \tan\left(-\frac{kL}{2} + \varphi\right) \\ \\ \frac{k}{\kappa} = -\tan\left(\frac{kL}{2} + \varphi\right) \end{array} \right| \tag{2.133}$$

solve for φ:

$$\left| \begin{array}{c} \varphi = \frac{kL}{2} + \arctan\frac{k}{\kappa} \\ \\ \varphi = -\frac{kL}{2} - \arctan\frac{k}{\kappa} + n\pi \end{array} \right|$$

Add and subtract both equations to obtain

$$\left| \begin{array}{c} \varphi = \frac{n\pi}{2} \\ \\ \arctan\frac{k}{\kappa} = -\frac{kL}{2} + \frac{n\pi}{2} \end{array} \right| \tag{2.134}$$

transcendental equation determines the quantization of energy levels

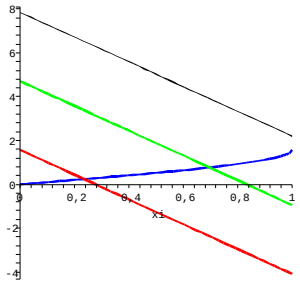
- graphical analysis:

$$\begin{aligned} \text{define} \qquad \zeta &= \sqrt{\frac{\varepsilon}{U}}\,, \quad (0 < \zeta \leq 1) \\ K &= \sqrt{U} \end{aligned}$$

eq. (2.134) can be written as

$$\frac{n\pi}{2} - \frac{\zeta K L}{2} = \arcsin\zeta \tag{2.135}$$

solutions: intercept points of straight line and arcsin function:



$\longrightarrow$ n eigenvalues exist if

$(n-1)\pi \leq \sqrt{UL^2} < n\pi$

(at least one for $n = 1$)

quantization :

$$\begin{aligned} k &\longrightarrow k_n \\ \kappa &\longrightarrow \kappa_n \\ A, C, D &\longrightarrow A_n, C_n, D_n \end{aligned}$$

- eigenfunctions:

  eqs. (2.129) + (2.130) together with $\varphi = \frac{n\pi}{2}$ (eq. (2.134)) yield:

$$\left| \begin{array}{l} \frac{A_n}{C_n} = e^{\frac{\kappa_n L}{2}} \sin\left(-\frac{k_n L}{2} + \frac{n\pi}{2} \right) \\ \\ \frac{D_n}{C_n} = e^{\frac{\kappa_n L}{2}} \sin\left(\frac{k_n L}{2} + \frac{n\pi}{2} \right) \end{array} \right| \tag{2.136}$$

  Distinguish n even and n odd:

$$\begin{array}{lllll} n \text{ even}: & \hookrightarrow & A_n = -D_n & & \\ & \hookrightarrow & C_n = \pm \dfrac{A_n e^{\frac{-\kappa_n L}{2}}}{\sin \frac{k_n L}{2}} & + \text{ for } n = 2, 6, 10, ... \\ & & & - \text{ for } n = 4, 8, 12, ... \end{array}$$

$$\text{solution}: \quad \psi_{\varepsilon_n}(x) = \begin{cases} A_n e^{\kappa_n x} & x < -\frac{L}{2} \\ -\frac{A_n e^{\frac{-\kappa_n L}{2}}}{\sin \frac{k_n L}{2}} \sin k_n x & -\frac{L}{2} \leq x \leq \frac{L}{2} \\ -A_n e^{-\kappa_n x} & x > \frac{L}{2} \end{cases}$$

$$\begin{array}{lllll} n \text{ odd}: & \hookrightarrow & A_n = D_n & & \\ & \hookrightarrow & C_n = \pm \dfrac{A_n e^{\frac{-\kappa_n L}{2}}}{\cos \frac{k_n L}{2}} & + \text{ for } n = 1, 5, 9, ... \\ & & & - \text{ for } n = 3, 7, 11, ... \end{array}$$

$$\text{solution}: \quad \psi_{\varepsilon_n}(x) = \begin{cases} A_n e^{\kappa_n x} & x < -\frac{L}{2} \\ \frac{A_n e^{\frac{-\kappa_n L}{2}}}{\cos \frac{k_n L}{2}} \cos k_n x & -\frac{L}{2} \leq x \leq \frac{L}{2} \\ A_n e^{-\kappa_n x} & x > -\frac{L}{2} \end{cases}$$

A_n can be determined by

$$\begin{aligned}
\int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx &= 1 \\
&= A_n^2 \int_{-\infty}^{-\frac{L}{2}} e^{2\kappa_n x} \, dx + A_n^2 \int_{\frac{L}{2}}^{\infty} e^{-2\kappa_n x} \, dx \\
&\quad + A_n^2 \frac{e^{-\kappa_n L}}{\sin^2(\frac{k_n L}{2})} \int_{-\frac{L}{2}}^{\frac{L}{2}} \sin^2(k_n x) \, dx \\
&= A_n^2 \left\{ \frac{e^{-\kappa_n L}}{\kappa_n} + \frac{e^{-\kappa_n L}}{\sin^2(\frac{k_n L}{L})} \Big(\frac{L}{2} - \frac{1}{2k_n} \sin(k_n L) \Big) \right\} \\
\iff \quad A_n &= e^{\frac{\kappa_n L}{2}} \left[\frac{1}{\kappa_n} + \frac{\frac{L}{2} - \frac{1}{2k_n} \sin(k_n L)}{\sin^2(\frac{k_n L}{2})} \right]^{-\frac{1}{2}}
\end{aligned}$$

(same result is obtained for n odd)
$\longrightarrow$ structurally very similar to previous case ($U \to \infty$), but eigenfunctions enter (slightly) the classically forbidden regions I, III.

2) $\boxed{\varepsilon > U}$:

$$\begin{aligned}
\psi_I(x) &= e^{ik_1 x} + B e^{-ik_1 x} \, , \qquad k_1 = \sqrt{\varepsilon - U} \\
\psi_{II}(x) &= C e^{ik_2 x} + D e^{-ik_2 x} \, , \quad k_2 = \sqrt{\varepsilon} \\
\psi_{III}(x) &= E e^{ik_1 x}
\end{aligned}$$

(we have chosen $A = 1$, $F = 0$; cf. page 25)

$\longrightarrow$ 4 equations for 4 constants B, C, D, E follow from matching conditions
$\longrightarrow$ continuous spectrum (no restriction on ε)

- consider current densities and coefficients T, R (page 26)

$$\left.\begin{aligned}
j_{in} &= \tfrac{\hbar k_1}{m} \\
j_{ref} &= -|B|^2 \tfrac{\hbar k_1}{m} \\
j_{trans} &= |E|^2 \tfrac{\hbar k_1}{m}
\end{aligned}\right\} \quad \begin{aligned}
&R = |B|^2 \\
&T = |E|^2 \\
&(R + T = |B|^2 + |E|^2 = 1)
\end{aligned}$$

- matching conditions yield (after some calculation (see A.1))

$$\begin{aligned} E &= \frac{e^{-ik_1 L}}{\cos k_2 L - \frac{i}{2}\left(\frac{k_1}{k_2} + \frac{k_2}{k_1}\right)\sin k_2 L} \\ T &= \frac{1}{\cos^2 k_2 L + \frac{1}{4}\left(\frac{k_1}{k_2} + \frac{k_2}{k_1}\right)^2 \sin^2 k_2 L} \end{aligned} \tag{2.137}$$

$$T = 1 \quad \text{if} \quad \cos^2 k_2 L = 1\ , \quad \sin^2 k_2 L = 0 \quad \hookrightarrow \quad k_2 = \frac{n\pi}{L}$$

(cf. eq. (2.120)) De Broglie wavelength $\lambda_B = \frac{2\pi}{k_2^{\max}} = \frac{2L}{n}$ is adapted to width of the well (cf. Sec. (2.4.2d))
$\longrightarrow$ one can show that a particle (represented by a narrow WP) with wave number close to $k_2 = \frac{n\pi}{L}$ stays in II for 'a long time' (significantly longer than a classical particle) before it moves on. (it is 'quasi-bound' $\longleftrightarrow$ resonance phenomenon)

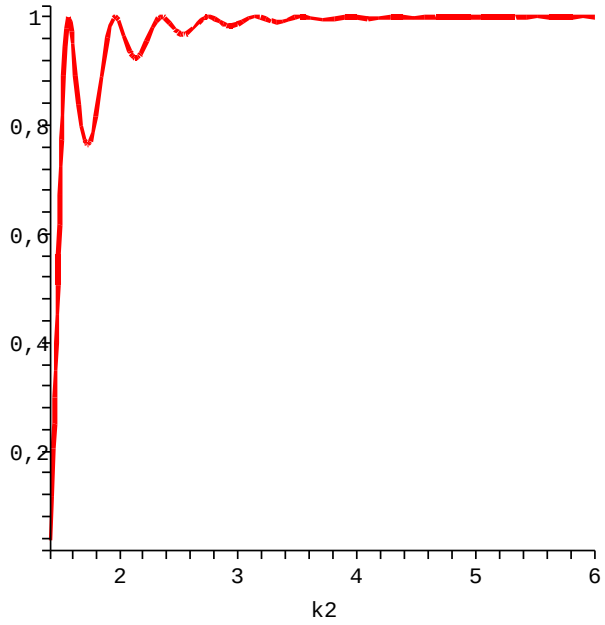


Figure 2.5: Transmission coefficient

- Transition from potential well to barrier

$$\begin{aligned} \text{well :} \qquad & k_1 = \sqrt{\varepsilon - U} \\ & k_2 = \sqrt{\varepsilon} \end{aligned}$$

$$\begin{aligned} \text{barrier :} \qquad & k_1 = \sqrt{\varepsilon - U} \\ & k_2 = \sqrt{\varepsilon - 2U} \;=\; i\sqrt{2U - \varepsilon} \;\equiv\; i\kappa \end{aligned}$$

i.e. replace in eq. (2.137) k_2 by $i\kappa$

$$\hookrightarrow \quad T \;=\; \frac{1}{\cosh^2 \kappa L + \frac{1}{4}\left(\frac{\kappa}{k_1} - \frac{k_1}{\kappa}\right)^2 \sinh^2 \kappa L}$$

this is the transmission coefficient for **tunneling** through a rectangular barrier.

f) Summary: quantum effects
- spreading of (free) WPs
- splitting of WPs: T, R
- WPs can enter + penetrate classically forbidden regions $\longrightarrow$ delayed reflection, tunnel effect
- bound states in wells are quantized; zero-point motion + energy
- scattering at potential wells: resonances

$\longrightarrow$ all items are rather general phenomena (not at all specific for our simple models!)

Chapter 3

Formalism of Quantum Mechanics

3.1 Mathematical framework

Wave mechanics is based on the principle of superposition. Mathematically, this implies that wave functions are vectors.

3.1.1 (State-) vectors and their linear space

a) Definition: vector space $\mathcal{H}$ (over $\mathbb{C}$)

denote ("ket") vectors as $|\psi\rangle$ (the symbol $|\ \rangle$ was introduced by Dirac)

A vector space is a set of vectors with two composition laws:

(i) summation of vectors:

$$\begin{aligned} + :\ \ & \mathcal{H} \times \mathcal{H} \longrightarrow \mathcal{H} \\ & |\psi_1\rangle\ + |\psi_2\rangle\ =\ |\psi\rangle\quad \in\ \mathcal{H} \end{aligned}$$

$\mathcal{H}$ is abelian group with respect to $+$, i.e.:

- $\Big(|\psi_1\rangle\ + |\psi_2\rangle\Big) + |\psi_3\rangle\ =\ |\psi_1\rangle\ +\ \Big(|\psi_2\rangle + |\psi_3\rangle\Big)$
- $\exists$ neutral element $|0\rangle\ \in\ \mathcal{H}$

$$|\psi\rangle\ + |0\rangle\ =\ |\psi\rangle\ ,\quad (\forall\ |\psi\rangle\quad |\psi\rangle\quad \in\ \mathcal{H})$$

- $\forall\ |\psi\rangle \in\ \mathcal{H}\ ,\quad \exists\quad |\psi'\rangle\ \in\ \mathcal{H}$:

$$\begin{aligned} |\psi\rangle + |\psi'\rangle\ &=\ |0\rangle \\ \longrightarrow\quad |\psi'\rangle\ &\equiv\ |-\psi\rangle \qquad \text{(inverse element)} \end{aligned}$$

- 'abelian': $\Longleftrightarrow\ |\psi_1\rangle + |\psi_2\rangle = |\psi_2\rangle + |\psi_1\rangle$

(ii) multiplication with $\alpha \in \mathbb{C}$:

$$\begin{aligned} \odot : \quad & \mathbb{C} \times \mathcal{H} \longrightarrow \mathcal{H} \\ & \alpha|\psi\rangle = |\alpha\psi\rangle \quad \in \mathcal{H} \end{aligned}$$

- $(\alpha_1 + \alpha_2)|\psi\rangle = \alpha_1|\psi\rangle + \alpha_2|\psi\rangle$
- $\alpha_1\Big(|\psi_1\rangle + |\psi_2\rangle\Big) = \alpha_1|\psi_1\rangle + \alpha_1|\psi_2\rangle$
- $(\alpha_1\alpha_2)|\psi\rangle = \alpha_1\Big(\alpha_2|\psi\rangle\Big)$
- $1 \cdot |\psi\rangle = |\psi\rangle$

principle of superposition: $|\psi_i\rangle \in \mathcal{H}\,, \quad \alpha_i \in \mathbb{C}\,, \quad i = 1, ..., N$

$$\hookrightarrow \quad |\psi\rangle = \sum_{i=1}^{N} \alpha_i |\psi_i\rangle \quad \in \mathcal{H}$$

b) Definition: scalar (inner, dot) product in $\mathcal{H}$

$$\begin{aligned} \mathcal{H} \times \mathcal{H} \quad &\longrightarrow \quad \mathbb{C} \\ |\psi_1\rangle, |\psi_2\rangle \quad &\longmapsto \quad \underbrace{\langle\psi_1|\psi_2\rangle}_{\text{"bracket"}} \quad \in \mathbb{C} \end{aligned}$$

- $\langle\psi_1|\psi_2 + \psi_3\rangle = \langle\psi_1|\psi_2\rangle + \langle\psi_1|\psi_3\rangle$
- $\langle\psi_1|\alpha\psi_2\rangle = \alpha\langle\psi_1|\psi_2\rangle$
- $\langle\psi_1|\psi_2\rangle^* = \langle\psi_2|\psi_1\rangle$
- $\langle\psi|\psi\rangle \geq 0\,; \quad \langle\psi|\psi\rangle = 0 \quad \Longleftrightarrow \quad |\psi\rangle = |0\rangle$
  $(\langle\psi|\psi\rangle \in \mathbb{R}$ follows from $\langle\psi_1|\psi_2\rangle^* = \langle\psi_2|\psi_1\rangle)$

a complex vector space with a scalar product is called unitary space or prehilbert space

$\longrightarrow$ consequences:

- $\langle\psi_1 + \psi_2|\psi_3\rangle = \langle\psi_1|\psi_3\rangle + \langle\psi_2|\psi_3\rangle$
- $\langle\alpha\psi_1|\psi_2\rangle = \alpha^*\langle\psi_1|\psi_2\rangle$

The objects "$\langle\ |$" are called "bra" (vectors). They are not elements of $\mathcal{H}$, but form another vector space, namely the so-called dual vector space $\mathcal{H}^*$ of $\mathcal{H}$.

obvious properties :

$$\begin{aligned} \langle\alpha\psi| &= \alpha^*\langle\psi| \\ \langle\psi_1 + \psi_2| &= \langle\psi_1| + \langle\psi_2| \end{aligned}$$

Some remarks:

- norm of a vector: $||\psi|| \;:=\; \sqrt{\langle\psi|\psi\rangle}$
- Schwarz's inequality: $|\langle\psi_1|\psi_2\rangle| \;\leq\; ||\psi_1||\;||\psi_2||$
- "orthogonality": $\Longleftrightarrow \quad \langle\psi_1|\psi_2\rangle = 0$
- "orthonormality": $\Longleftrightarrow \quad \langle\psi_1|\psi_2\rangle = 0$
  $\wedge\; \langle\psi_1|\psi_1\rangle = \langle\psi_2|\psi_2\rangle = 1\;, \quad$ i.e. $\langle\psi_i|\psi_j\rangle = \delta_{ij}$
- quadratically integrable functions form unitary space.
  Vector properties can be easily checked.

$$\begin{aligned} &\text{scalar product} \qquad \langle\psi_1|\psi_2\rangle \;&:=\; &\int_{-\infty}^{\infty} \psi_1^*(x)\psi_2(x)\;dx \\ &\text{normalization} \qquad\quad \langle\psi|\psi\rangle \;&=\; &\int_{-\infty}^{\infty} |\psi(x)|^2\;dx \end{aligned}$$

This can be generalized to functions $\Psi(\mathbf{r}_1...\mathbf{r}_N)$:

$$\langle\Psi_1|\Psi_2\rangle \;:=\; \int \Psi_1^*(\mathbf{r}_1...\mathbf{r}_N)\Psi_2(\mathbf{r}_1...\mathbf{r}_N)\;d^3\mathbf{r}_1...d^3\mathbf{r}_N$$

c) Basis states and systems

i) finite vector space $\dim\mathcal{H} = N$
a set of vectors $\left\{|\psi_i\rangle\;,\quad i=1,...,N\;\right\}$ is linearly independent:

$$\Longleftrightarrow \quad \sum_{i=1}^{N}\alpha_i|\psi_i\rangle \;= 0 \qquad \text{only if} \quad \alpha_1=\alpha_2=...=\alpha_N=0$$

$$\Longrightarrow \quad \forall\;\psi\;\in\;\mathcal{H}: \quad |\psi\rangle \;= \sum_{i=1}^{N}\alpha_i|\psi_i\rangle\;, \quad \left\{|\psi_i\rangle\right\}:\;''\text{basis}''$$

a basis $\left\{|\varphi_i\rangle\right\}$ is called orthonormal if

$$|\psi\rangle = \sum_{i=1}^{N}\alpha_i|\varphi_i\rangle$$

$$\langle\varphi_i|\varphi_j\rangle = \delta_{ij}\;, \quad i,j=1,...,N$$

ii) $\dim\mathcal{H} \longrightarrow \infty$
definition of a linearly independent set persists, but we have to clarify what $|\psi\rangle = \sum_{i=1}^{\infty}\alpha_i|\varphi_i\rangle$ shall mean, i.e., we need to establish the notion of convergence of a sequence $|\psi_N\rangle = \sum_{i=1}^{N}\alpha_i|\varphi_i\rangle \;\overset{N\to\infty}{\longrightarrow}\; |\psi\rangle$

- Let's define a "distance" (metric):

$$\begin{aligned} d(\psi, \psi_N) &\equiv ||\psi - \psi_N|| \\ &= \sqrt{\langle \psi - \psi_N | \psi - \psi_N \rangle} \overset{N\to\infty}{\longrightarrow} 0 \end{aligned}$$

  $\longrightarrow$ this is a well-defined notion of convergence

- Cauchy sequence $\{|\psi_N\rangle\} :\Longleftrightarrow \quad \forall\, \varepsilon > 0 \quad \exists\, N \in \mathbb{N}:$

$$||\psi_n - \psi_m|| < \varepsilon\,, \quad \forall\, n, m > N$$

- a unitary space is called complete if all Cauchy sequences converge, i.e., $|\psi_N\rangle \overset{N\to\infty}{\longrightarrow} |\psi\rangle \in \mathcal{H}$

d) Hilbert space $:\Longleftrightarrow$ unitary space which is complete with respect to norm $||\psi|| = \sqrt{\langle \psi | \psi \rangle}$

- separable Hilbert space $:\Longleftrightarrow \quad \forall\, |\psi\rangle \in \mathcal{H}\ \exists$ countable sequence $\{|\varphi_n\rangle\}$ such that $|\psi\rangle = \sum_{n=1}^{\infty} \alpha_n |\varphi_n\rangle$ (the basis may be orthonormal ("ONB") $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$)

> The quadratically integrable functions $\Psi(\mathbf{r}_1 ... \mathbf{r}_N)$ in configuration space $(\mathbf{r}_1 ... \mathbf{r}_N)$ form a separable Hilbert space with $\dim \mathcal{H} = \infty$

  $\longrightarrow$ QM states can be characterized as Hilbert space vectors

- example for an orthonormal basis in such a space ($''L^2(-\infty, \infty)''$)

$$\varphi_n(x) = \frac{1}{\sqrt{2^n n! \sqrt{\pi}}}\, e^{-\frac{x^2}{2}} H_n(x), \quad n = 0, 1, ...$$

(Hermite's functions)

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2} \quad \text{Hermite's polynomials}$$

$$\Longrightarrow \quad \psi(x) = \sum_{n=0}^{\infty} \alpha_n \varphi_n(x)$$

for all quadratically integrable functions $\psi(x)$

$$\hookrightarrow \quad \int_{-\infty}^{\infty} \varphi_m(x) \psi(x)\, dx = \langle \varphi_m | \psi \rangle$$

$$= \sum_{n=0}^{\infty} \alpha_n \int_{-\infty}^{\infty} \underbrace{\varphi_m(x) \varphi_n(x)\, dx}_{=\delta_{mn}} = \alpha_m$$

Making use of Dirac's notation we can write

$$|\psi\rangle = \sum_n \alpha_n |\varphi_n\rangle \tag{3.1}$$

$$\hookrightarrow \quad \langle\varphi_m|\psi\rangle = \alpha_m \tag{3.2}$$

- scalar product with respect to ONB:

$$\langle\psi_1|\psi_2\rangle = \sum \alpha_m^{(1)*}\alpha_n^{(2)} \underbrace{\langle\varphi_m|\varphi_n\rangle}_{=\delta_{mn}} = \sum \langle\psi_1|\varphi_m\rangle\langle\varphi_m|\psi_2\rangle$$

in particular:

$$\langle\psi|\psi\rangle = \sum_{n,m} \alpha_m^* \alpha_n \underbrace{\langle\varphi_m|\varphi_n\rangle}_{=\delta_{mn}} = \sum_n |\alpha_n|^2 \tag{3.3}$$

(Parseval's relation: characterizes a complete basis set)
Short hand notation: $|\varphi_n\rangle \equiv |n\rangle$

3.1.2 (linear) Operators

Operators are <u>linear</u> maps: $|\varphi\rangle \xrightarrow{\hat{A}} |\psi\rangle = \hat{A}|\varphi\rangle = |\hat{A}\varphi\rangle$:

$$\hat{A}(|\psi_1\rangle + |\psi_2\rangle) = \hat{A}|\psi_1\rangle + \hat{A}|\psi_2\rangle \tag{3.4}$$

$$\hat{A}(\alpha|\psi\rangle) = \alpha\hat{A}|\psi\rangle \tag{3.5}$$

a) Sum of operators and multiplication with scalar

$$(\hat{A}+\hat{B})|\psi\rangle := \hat{A}|\psi\rangle + \hat{B}|\psi\rangle\ , \qquad \forall\ |\psi\rangle \in \mathcal{H}$$
$$(\alpha\hat{A})|\psi\rangle := \alpha(\hat{A}|\psi\rangle)\ , \qquad \forall\ \alpha \in \mathbb{C}$$

$\longrightarrow$ the set of linear operators forms a vector space! (check the vector space axioms!)

b) Product of operators

$$\hat{A}\hat{B}|\psi\rangle := \hat{A}(\hat{B}|\psi\rangle) = \hat{A}|\hat{B}\psi\rangle\ , \quad \forall\ |\psi\rangle \in \mathcal{H}$$

("apply $\hat{B}$ first, and then $\hat{A}$")

<u>properties:</u>

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$$
$$\alpha(\hat{A}\hat{B}) = (\alpha\hat{A})\hat{B} = \hat{A}(\alpha\hat{B})$$
$$\hat{A}\hat{1} = \hat{1}\hat{A} = \hat{A}\ , \qquad (\hat{1} : \text{"unity" operator})$$
$$\hat{A}(\hat{B}+\hat{C}) = \hat{A}\hat{B} + \hat{A}\hat{C}$$
$$(\hat{A}+\hat{B})\hat{C} = \hat{A}\hat{C} + \hat{B}\hat{C}$$

but:

- not every operator $\hat{A}$ has an inverse operator $\hat{A}^{-1}$, such that $\hat{A}\hat{A}^{-1} = \hat{A}^{-1}\hat{A} = \hat{1}$
- in general $\hat{A}\hat{B} \neq \hat{B}\hat{A}$

$$\longrightarrow \text{ commutator} \qquad [\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{3.6}$$

(a very important object for QM!)
some rules (easy to prove):

$$\begin{aligned}
[\hat{A}, \hat{A}] &= [\hat{A}, \hat{1}] = 0 \\
[\hat{A}, \hat{B}] &= -[\hat{B}, \hat{A}] \\
[\hat{A}, \beta\hat{B}] &= \beta[\hat{A}, \hat{B}] \\
[\hat{A}, \hat{B} + \hat{C}] &= [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \\
[\hat{A}, \hat{B}\hat{C}] &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \\
0 &= [\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]]
\end{aligned}$$

c) Operator functions

With sum and product of operators we can define

$$f(\hat{A}) = \alpha_0\hat{1} + \alpha_1\hat{A} + \alpha_2\hat{A}^2 + \ldots$$

$$\text{e.g.:} \qquad e^{\hat{A}} := \sum_{n=0}^{\infty} \frac{\hat{A}^n}{n!} \tag{3.7}$$

note that $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}$ only if $[\hat{A}, \hat{B}] = 0$

d) Special operators

- Inverse operator: if it exists it is defined via

$$\begin{aligned}
|\chi\rangle &= \hat{A}|\psi\rangle \\
\hookrightarrow \quad |\psi\rangle &= \hat{A}^{-1}|\chi\rangle \\
\Longrightarrow \quad \hat{A}\hat{A}^{-1} &= \hat{A}^{-1}\hat{A} = \hat{1} \\
(\hat{A}^{-1})^{-1} &= \hat{A} \\
(\alpha\hat{A})^{-1} &= \frac{1}{\alpha}\hat{A}^{-1} \\
(\hat{A}\hat{B})^{-1} &= \hat{B}^{-1}\hat{A}^{-1}
\end{aligned} \tag{3.8}$$

- Adjoint operator $\hat{A}^\dagger$
  consider scalar product $\langle\chi|\zeta\rangle \equiv \langle\chi|\hat{A}\psi\rangle$

$\hat{A}^\dagger$ is defined by property:

$$\langle\chi|\hat{A}\psi\rangle = \langle\hat{A}^\dagger\chi|\psi\rangle = \langle\psi|\hat{A}^\dagger\chi\rangle^* \tag{3.9}$$

properties (easy to verify) :
$$\begin{aligned}(\hat{A}^\dagger)^\dagger &= \hat{A}\\ (\alpha\hat{A})^\dagger &= \alpha^*\hat{A}^\dagger\\ (\hat{A}+\hat{B})^\dagger &= \hat{A}^\dagger+\hat{B}^\dagger\\ (\hat{A}\hat{B})^\dagger &= \hat{B}^\dagger\hat{A}^\dagger\end{aligned}$$

note the "conjugation relations"

c-numbers	α^*	$\longleftrightarrow$	α
vectors	$\langle\psi\|$	$\longleftrightarrow$	$\|\psi\rangle$
operators	$\hat{A}^\dagger$	$\longleftrightarrow$	$\hat{A}$

(but note that $\langle\psi|$ and $|\psi\rangle$ are elements of different spaces)

- Self-adjoint (hermitian) operator $:\Longleftrightarrow \hat{A} = \hat{A}^\dagger$
  properties:
  - $\langle\hat{A}^\dagger\chi|\psi\rangle = \langle\hat{A}\chi|\psi\rangle = \langle\chi|\hat{A}\psi\rangle$

    $$\text{write} \quad = \langle\chi|\hat{A}|\psi\rangle \tag{3.10}$$

    (we will use this notation from now on for all operators. In general, it is understood that $\hat{A}$ acts to the right.)
  - $\langle\psi|\hat{A}|\psi\rangle \in \mathbb{R}$
  - $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger\hat{A}^\dagger = \hat{B}\hat{A} = \hat{A}\hat{B} \quad$ only if $\quad [\hat{A},\hat{B}] = 0$
  - $[\hat{A},\hat{B}]^\dagger = [\hat{B},\hat{A}] = -[\hat{A},\hat{B}]$
- Unitary operator $:\Longleftrightarrow \quad \hat{U}^\dagger \equiv \hat{U}^{-1}$

  $$\hookrightarrow \quad \hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{1} \tag{3.11}$$

  properties:
  - $|\psi'\rangle := U|\psi\rangle\,, \quad |\varphi'\rangle := \hat{U}|\varphi\rangle$

    $$\Longrightarrow \quad \langle\varphi'|\psi'\rangle = \langle\hat{U}\varphi|\hat{U}\psi\rangle = \langle\varphi|\hat{U}^\dagger\hat{U}|\psi\rangle = \langle\varphi|\psi\rangle$$
  - $\hat{W} = \hat{U}\hat{V} \quad$ and $\quad \hat{U},\hat{V}$ unitary

    $$\Longrightarrow \quad \hat{W}^{-1} = (\hat{U}\hat{V})^{-1} = \hat{V}^{-1}\hat{U}^{-1} = \hat{V}^\dagger\hat{U}^\dagger = (\hat{U}\hat{V})^\dagger = \hat{W}^\dagger$$

    ($\rightarrow$ unitary operators form a group)

- Projection operators (projectors)
  define 'elementary projector' via

$$\hat{P}_n|\psi\rangle := |n\rangle\langle n|\psi\rangle \ , \qquad (\text{assume } \langle n|n\rangle = 1)$$

$$\longrightarrow \quad \text{i.e.} \qquad \hat{P}_n = |n\rangle\langle n| \tag{3.12}$$

  properties: (easy to prove)

$$\left.\begin{aligned} \hat{P}_n &= \hat{P}_n^\dagger \\ \hat{P}_n^2 &= \hat{P}_n \end{aligned}\right\} \text{ these are the defining properties of 'general' projectors}$$

$$\Longrightarrow \quad \hat{P}_m\hat{P}_n = \delta_{mn}\hat{P}_n$$

  further examples of projectors:

$$\hat{P} = \sum_{n=1}^{N} |n\rangle\langle n| \ , \qquad (\text{i.e., show } \hat{P} = \hat{P}^\dagger \ , \quad \hat{P}^2 = \hat{P})$$

$$\hookrightarrow \quad \hat{P}|\psi\rangle = \sum_{n=1}^{N} |n\rangle\langle n|\psi\rangle = \sum_{n=1}^{N} \alpha_n|n\rangle$$

$$\hat{P}_\infty = \sum_{n=1}^{\infty} |n\rangle\langle n| \equiv \hat{1} \ , \quad \text{"completeness relation"} \tag{3.13}$$

$$\hookrightarrow \quad |\psi\rangle = \sum_{n=1}^{\infty} |n\rangle\langle n|\psi\rangle = \sum_{n=1}^{\infty} \alpha_n|n\rangle$$

  The completeness relation (decomposition of the unity operator) is equivalent to Parseval's relation (3.3):

$$\langle\psi|\psi\rangle = \langle\psi|\hat{1}|\psi\rangle = \sum_n \langle\psi|n\rangle\langle n|\psi\rangle = \sum_n |\alpha_n|^2$$

3.1.3 Representation of vectors and operators

$\longrightarrow$ insert unity operator at appropriate places:

a) Vectors

$$|\psi\rangle = \hat{1}|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle \tag{3.14}$$

$$|\psi\rangle \ \longrightarrow \ \begin{pmatrix} \langle 1|\psi\rangle \\ \langle 2|\psi\rangle \\ \vdots \end{pmatrix} = \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \end{pmatrix}$$

$$\langle\phi| = \langle\phi|\hat{1} = \sum_n \langle\phi|n\rangle\langle n| \tag{3.15}$$

$$\begin{aligned} \langle\phi| \;\longrightarrow\; & (\langle\phi|1\rangle, \langle\phi|2\rangle, \ldots) \\ = \; & (\langle 1|\phi\rangle^*, \langle 2|\phi\rangle^*, \ldots) \\ = \; & (\beta_1^*, \beta_2^*, \ldots) \end{aligned}$$

scalar product

$$\langle\phi|\psi\rangle = \sum_n \langle\phi|n\rangle\langle n|\psi\rangle = (\beta_1^*\beta_2^* \ldots) \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \end{pmatrix}$$

$$= \beta_1^*\alpha_1 + \beta_2^*\alpha_2 + \ldots = \sum_n \beta_n^*\alpha_n \tag{3.16}$$

b) Operators

$$\hat{A} = \hat{1}\hat{A}\hat{1} = \sum_{m,n} |m\rangle\langle m|\hat{A}|n\rangle\langle n| \tag{3.17}$$

"matrix elements" $A_{mn} := \langle m|\hat{A}|n\rangle \;\in\; \mathbb{C}$

$$\hat{A} \;\longrightarrow\; \begin{pmatrix} \langle 1|\hat{A}|1\rangle & \langle 1|\hat{A}|2\rangle & \ldots \\ \langle 2|\hat{A}|1\rangle & \langle 2|\hat{A}|2\rangle & \ldots \\ \vdots & \ddots & \end{pmatrix}$$

- $\langle m|\hat{A}|\psi\rangle = \sum_n \langle m|\hat{A}|n\rangle\langle n|\psi\rangle = \sum_n A_{mn}\alpha_n$
  $\longrightarrow$ the representation of the vector $\hat{A}|\psi\rangle$ has to be calculated as a matrix-vector product
- $\langle\phi|\hat{A}|n\rangle = \sum_m \langle\phi|m\rangle\langle m|\hat{A}|n\rangle = \sum_m \beta_m^* A_{mn}$
- general matrix element

$$\langle\phi|\hat{A}|\psi\rangle = \langle\phi|\hat{1}\hat{A}\hat{1}|\psi\rangle = \sum_{mn} \beta_m^* A_{mn}\alpha_n$$

$$(\beta_1^*\beta_2^* \ldots) \begin{pmatrix} A_{11} & A_{12} & \ldots \\ A_{21} & A_{22} & \ldots \\ \vdots & \ddots & \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \end{pmatrix}$$

- operator product

$$\hat{A}\hat{B} = \hat{1}\hat{A}\hat{1}\hat{B}\hat{1} = \sum_{mk} |m\rangle \underbrace{\sum_n A_{mn}B_{nk}}_{\text{product of matrices}} \langle k| \tag{3.18}$$

- adjoint operator

$$(\hat{A}^\dagger)_{mn} = \langle m|\hat{A}^\dagger|n\rangle = \langle n|\hat{A}|m\rangle^* = A^*_{nm} = A^\dagger_{mn} \tag{3.19}$$

  $\longrightarrow$ adjoint operator is represented by adjoint matrix

- hermitian operator $\hat{A} = \hat{A}^\dagger$

$$A_{mn} = \langle m|\hat{A}|n\rangle = \langle n|\hat{A}|m\rangle^* = A^*_{nm} \tag{3.20}$$

c) Change of representation

consider two different ONB's

$$\begin{aligned} \left\{|u_i\rangle\ ;\quad i=1,...\right\}\ , &\quad \langle u_i|u_k\rangle &= \delta_{ik} \\ \left\{|v_j\rangle\ ;\quad j=1,...\right\}\ , &\quad \langle v_j|v_l\rangle &= \delta_{jl} \end{aligned}$$

$$\begin{aligned} |\psi\rangle &= \sum_i |u_i\rangle\langle u_i|\psi\rangle \\ &= \sum_{ij} |v_j\rangle\langle v_j|u_i\rangle\langle u_i|\psi\rangle = \sum_j |v_j\rangle\langle v_j|\psi\rangle \end{aligned}$$

$$\hookrightarrow \quad \langle v_j|\psi\rangle = \sum_i \langle v_j|u_i\rangle\langle u_i|\psi\rangle = \sum_i U_{ji}\langle u_i|\psi\rangle \tag{3.21}$$

$\longrightarrow$ transformation is mediated by unitary matrix $\underline{\underline{U}}$!

proof:

$$\begin{aligned} \sum_k U^\dagger_{ik}U_{kj} &= \sum_k U^*_{ki}U_{kj} = \sum_k \langle v_k|u_i\rangle^*\langle v_k|u_j\rangle \\ &= \sum_k \langle u_i|v_k\rangle\langle v_k|u_j\rangle = \langle u_i|u_j\rangle = \delta_{ij} \end{aligned}$$

$\longrightarrow$ if ONB's $\left\{|u_i\rangle\right\}$, $\left\{|v_j\rangle\right\}$ have the same index set one can extract an operator $\hat{U}$ that has the matrix elements $U_{ji} = \langle v_j|u_i\rangle$

$$\hookrightarrow \quad \hat{U} = \sum_k |u_k\rangle\langle v_k|\ , \qquad (\hat{U}^{-1} = \hat{U}^\dagger) \tag{3.22}$$

proof:

$$\begin{aligned} U_{ji} &= \langle v_j|\hat{U}|v_i\rangle = \sum_k \langle v_j|u_k\rangle \underbrace{\langle v_k|v_i\rangle}_{\delta_{ki}} \\ &= \langle v_j|u_i\rangle = \langle u_j|\hat{U}|u_i\rangle \\ &= \sum_k \langle u_j|u_k\rangle\langle v_k|u_i\rangle = \langle v_j|u_i\rangle \end{aligned}$$

- transformation of operators

$$\begin{aligned}\langle u_i|\hat{A}|u_j\rangle &= \sum_{kl}\langle u_i|v_k\rangle\langle v_k|\hat{A}|v_l\rangle\langle v_l|u_j\rangle \\ &= \sum_{kl} U^{\dagger}_{ik}\langle v_k|\hat{A}|v_l\rangle U_{lj} \end{aligned} \tag{3.23}$$

3.1.4 Non-orthogonal basis sets

Sometimes it is useful to consider a basis $\{|\varphi_i\rangle\ , \quad i=1,...\}$ which is (complete, but) not orthonormal, i.e.,

$$S_{ij} \equiv \langle\varphi_i|\varphi_j\rangle \neq \delta_{ij}$$

S_{ij} = 'overlap matrix' is positive definite and hermitian
$(S_{ij} = S^*_{ji})$ $\rightarrow$ inverse exists and is also hermitian!

A projector onto an $N-$dimensional subspace $\{|\varphi_1\rangle \dots |\varphi_N\rangle\}$ is given as

$$\hat{P} = \sum_{ij=1}^{N} |\varphi_i\rangle S^{-1}_{ij}\langle\varphi_j| \tag{3.24}$$

proof:
i) $\hat{P} = \hat{P}^{\dagger}$

$$\begin{aligned} \hookrightarrow \quad \langle\chi|\hat{P}|\psi\rangle &= \sum_{ij=1}^{N}\langle\chi|\varphi_i\rangle S^{-1}_{ij}\langle\varphi_j|\psi\rangle \\ &= \sum_{ij}\langle\varphi_i|\chi\rangle^*\left(S^{-1}_{ji}\right)^*\langle\psi|\varphi_j\rangle^* \\ &= \Big(\sum_{ij}\langle\psi|\varphi_j\rangle S^{-1}_{ji}\langle\varphi_i|\chi\rangle\Big)^* \\ &= \langle\psi|\hat{P}|\chi\rangle^* = \langle\hat{P}\chi|\psi\rangle \end{aligned}$$

ii) $\hat{P}^2 = \hat{P}$

$$\begin{aligned} \hookrightarrow \quad \hat{P}^2 &= \sum_{ijkl}|\varphi_i\rangle S^{-1}_{ij}\langle\varphi_j|\varphi_k\rangle S^{-1}_{kl}\langle\varphi_l| \\ &= \sum_{ikl}|\varphi_i\rangle \underbrace{\Big(\sum_j S^{-1}_{ij}S_{jk}\Big)}_{=\delta_{ik}} S^{-1}_{kl}\langle\varphi_l| \\ &= \sum_{il}|\varphi_i\rangle S^{-1}_{il}\langle\varphi_l| \quad = \quad \hat{P} \end{aligned}$$

$$\begin{aligned} \Longrightarrow \quad \hat{1} &= \sum_{ij=1}^{\infty}|\varphi_i\rangle S^{-1}_{ij}\langle\varphi_j| \end{aligned} \tag{3.25}$$

- representation of a ket

$$\begin{aligned} |\psi\rangle &= \sum_{ij=1}^{\infty} |\varphi_i\rangle S_{ij}^{-1} \langle\varphi_j|\psi\rangle \equiv \sum_i c_i |\varphi_i\rangle \\ \hookrightarrow \quad c_i &= \sum_j S_{ij}^{-1} \langle\varphi_j|\psi\rangle \end{aligned}$$

- representation of an operator

$$\begin{aligned} \hat{A} = \hat{1}\hat{A}\hat{1} &= \sum_{ijkl} |\varphi_i\rangle S_{ij}^{-1} \langle\varphi_j|\hat{A}|\varphi_k\rangle S_{kl}^{-1} \langle\varphi_l| \\ &\equiv \sum_{il} |\varphi_i\rangle \tilde{A}_{il} \langle\varphi_l| \end{aligned}$$

$$\tilde{A}_{il} = \sum_{jk} S_{ij}^{-1} A_{jk} S_{kl}^{-1}$$

for $S_{ij} = \delta_{ij} = S_{ij}^{-1}$ the old expressions (3.14), (3.17) are reobtained.

3.1.5 Eigenvalue problem

$$\lhd \qquad \hat{A}|u_a\rangle = a|u_a\rangle \ , \qquad (|u_a\rangle \in \mathcal{H}) \tag{3.26}$$

Obviously it depends on the properties of $\hat{A}$ whether such an equation is fulfilled, i.e., whether eigenvectors $|u_{a_i}\rangle$ and eigenvalues a_i exist.

Insert $\hat{1}$ in (3.26):

$$\sum_k \hat{A}|k\rangle\langle k|u_a\rangle = a \sum_k |k\rangle\langle k|u_a\rangle \qquad || \ \langle l|$$

$$\hookrightarrow \quad \sum_k \Big(A_{lk} u_a^k - a\delta_{lk} u_a^k \Big) = 0 \tag{3.27}$$

for $\dim \mathcal{H} = N$ this homogeneous system of eqs. has a nontrivial solution if

$$\det(A_{lk} - \delta_{lk} a) = 0 \tag{3.28}$$

$\longrightarrow$ the roots of eq. (3.28) are the eigenvalues a_i, and inserting them into (3.27) yields the eigenvectors. The eigenvectors can be normalized: $\langle u_{a_i}|u_{a_i}\rangle = 1$

a) Eigenvalue problem for hermitian operators (non-degenerate case)

$$\hat{A}|u_{a_i}\rangle = a_i|u_{a_i}\rangle$$

non-degenerate case means that each eigenvector $|u_{a_i}\rangle$ corresponds to a different eigenvalue a_i (i.e. $a_i \neq a_j$ for $i \neq j$)

$$\begin{aligned} \hookrightarrow \quad \langle u_{a_j}|\hat{A}|u_{a_i}\rangle &= a_i\langle u_{a_j}|u_{a_i}\rangle \\ &= \langle \hat{A}u_{a_j}|u_{a_i}\rangle \\ &= \langle u_{a_i}|\hat{A}|u_{a_j}\rangle^* \\ &= a_j^*\langle u_{a_j}|u_{a_i}\rangle \end{aligned}$$

$$\iff \quad (a_i - a_j^*)\langle u_{a_j}|u_{a_i}\rangle = 0$$

i) $i = j$: $\quad \Longrightarrow a_i = a_i^* \quad \forall\ i$ (3.29)

$\longrightarrow$ all eigenvalues are real numbers!

ii) $i \neq j$: $\quad \Longrightarrow \langle u_{a_j}|u_{a_i}\rangle = 0$ (3.30)

$\longrightarrow$ eigenvectors are orthogonal!

further remarks:

- the eigenvectors of hermitian operators form ONBs in Hilbert space (disregarding some exceptions that will not be discussed):

$$\sum_{i=1}^{\infty} |u_{a_i}\rangle\langle u_{a_i}| = \hat{1}$$

- $\langle u_{a_j}|\hat{A}|u_{a_i}\rangle = a_i\delta_{ij}$ (3.31)

$$\longrightarrow \quad \text{diagonal matrix} \quad \hat{A} \longrightarrow \begin{pmatrix} a_1 & & & 0 \\ & a_2 & & \\ & & \ddots & \\ 0 & & & \ddots \end{pmatrix}$$

- $$\begin{aligned} a_i\delta_{ij} &= \sum_{kl}\langle u_{a_j}|l\rangle\langle l|\hat{A}|k\rangle\langle k|u_{a_i}\rangle \\ &= \sum_{kl} U_{jl}^{\dagger}A_{lk}U_{ki} \end{aligned}$$

  $\longrightarrow$ diagonalization is mediated by unitary transformation from representation $\{|k\rangle\}$ to representation $\{|u_{a_i}\rangle\}$ (cf. eq. (3.23))

- spectral representation of an operator $\hat{A} = \hat{A}^\dagger$:

$$\hat{A} = \hat{1}\hat{A}\hat{1} = \sum_i a_i |u_{a_i}\rangle\langle u_{a_i}| = \sum_i a_i \hat{P}_i \tag{3.32}$$

- $$\langle\psi|\hat{A}|\psi\rangle = \sum_i |\langle u_{a_i}|\psi\rangle|^2 \; a_i \tag{3.33}$$

- $$f(\hat{A}) = \alpha_0\hat{1} + \alpha_1\hat{A} + \alpha_2\hat{A}^2 + \ldots$$
$$\hookrightarrow \quad f(\hat{A})|u_{a_i}\rangle = f(a_i)|u_{a_i}\rangle \tag{3.34}$$

  $\longrightarrow$ i.e. operator function $f(\hat{A})$ has the same eigenvectors as $\hat{A}$

  Instead of a general proof: illustrate (3.34) for $\hat{A}^2$:

$$\begin{aligned} \hat{A}^2 &\overset{(3.32)}{=} \sum_{ij} |u_{a_j}\rangle \underbrace{\langle u_{a_j}|u_{a_i}\rangle}_{=\delta_{ij}} \langle u_{a_i}| a_i a_j \\ &= \sum_i a_i^2 |u_{a_i}\rangle\langle u_{a_i}| \end{aligned}$$

b) Eigenvectors of commuting operators (without degeneracies)

$$\begin{aligned} &\text{consider :} && \hat{A}|u_{a_i}\rangle &&= a_i|u_{a_i}\rangle \\ &\text{and} && [\hat{A},\hat{B}] &&= 0 \end{aligned}$$

$$\begin{aligned} \hookrightarrow \quad \hat{A}\hat{B}|u_{a_i}\rangle = \hat{B}\hat{A}|u_{a_i}\rangle &= a_i\hat{B}|u_{a_i}\rangle \\ \Longrightarrow \quad \hat{B}|u_{a_i}\rangle &= b_i|u_{a_i}\rangle \end{aligned}$$

on the other hand: assume that $\hat{A}, \hat{B}$ have the same complete set of eigenvectors, i.e.

$$\begin{aligned} \hat{A} &= \sum_i a_i |u_{a_i}\rangle\langle u_{a_i}| = \sum_i a_i \hat{P}_i \\ \hat{B} &= \sum_j b_j |u_{a_j}\rangle\langle u_{a_j}| = \sum_j b_j \hat{P}_j \end{aligned}$$

$$\Longrightarrow \quad \hat{A}\hat{B} = \sum_{ij} a_i \hat{P}_i b_j \hat{P}_j = \sum_{ij} b_j \hat{P}_j a_i \hat{P}_i = \hat{B}\hat{A} \;, \quad \text{(because } [\hat{P}_i, \hat{P}_j] = 0)$$

summary: operators $\hat{A}, \hat{B}$ have the same complete set of eigenvectors

$$\Longleftrightarrow \quad [\hat{A},\hat{B}] = 0$$

very important statement!

c) Degeneracy

$$\hat{A}|a_i^\mu\rangle = a_i|a_i^\mu\rangle \ , \quad \mu = 1, ..., N_i \tag{3.35}$$

(we use short-hand notation $|a_i^\mu\rangle \equiv |u_{a_i}^\mu\rangle$)

$\longrightarrow$ eigenvalue a_i is N_i-fold degenerate, i.e., N_i linearly independent eigenvectors $\left\{|a_i^\mu\rangle \ , \quad \mu = 1, ..., N_i\right\}$ exist. They span an N_i-dimensional subspace of Hilbert space ("eigenspace")($N_i \longrightarrow \infty$ is also possible)

$\longrightarrow$ they are not automatically orthogonal, but one can always orthogonalize them (e.g. by Gram-Schmidt procedure)

$$\hookrightarrow \quad \langle a_i^\mu | a_j^\nu\rangle = \delta_{ij}\delta_{\mu\nu} \tag{3.36}$$

- consider operator $\hat{B}$ which commutes with $\hat{A}$ (cf. page 54)

$$\hookrightarrow \quad \hat{A}\hat{B}|a_i^\mu\rangle = \hat{B}\hat{A}|a_i^\mu\rangle = a_i\hat{B}|a_i^\mu\rangle$$

i.e. vector $\hat{B}|a_i^\mu\rangle$ is eigenvector of $\hat{A}$ with eigenvalue a_i. This implies that $\hat{B}|a_i^\mu\rangle \in \left\{|a_i^1\rangle, ..., |a_i^{N_i}\rangle\right\}$
One can always find a transformation such that

$$\hat{B}|\tilde{a}_i^\mu\rangle = b_i^\mu|\tilde{a}_i^\mu\rangle$$

$\longrightarrow$ note that eigenvalues b_i^μ of $\hat{B}$ are not necessarily degenerate (like a_i); degeneracy may be lifted

summary: $[\hat{A}, \hat{B}] = 0 \quad \Longleftrightarrow \quad \hat{A}, \hat{B}$ have same (complete) set of eigenvectors, but degeneracies of eigenvalues can be different

- unity operator:

$$\sum_{i\mu} |a_i^\mu\rangle\langle a_i^\mu| = \hat{1} \tag{3.37}$$

- spectral representation:

$$\hat{A} = \sum_{i\mu} a_i|a_i^\mu\rangle\langle a_i^\mu| \tag{3.38}$$

(note that $\sum_{i\mu} \Longrightarrow \sum_{i=1}^{\infty}\sum_{\mu=1}^{N_i}$)

3.1.6 Continuous basis sets and spectra

(One) motivation: stationary Schrödinger equation has the form of an eigenvalue equation. We have seen that in some cases the 'spectrum of eigenvalues' is continuous ($\rightarrow$ scattering problems) and not discrete!
$\rightarrow$ we need to talk about continuous basis sets and spectra

- For $|\phi\rangle, |\psi\rangle \in \mathcal{H}$ ($\mathcal{H}$ separable) we can calculate the scalar product according to
$$\langle\phi|\psi\rangle = \langle\phi|\hat{1}|\psi\rangle = \sum_k \langle\phi|k\rangle\langle k|\psi\rangle = \sum_k \phi_k^* \psi_k$$
- On the other hand we have argued that
$$\langle\phi|\psi\rangle = \int_{-\infty}^{\infty} \phi^*(x)\psi(x)\, dx$$
is a legitimate scalar product for quadratically integrable wave functions (which form a separable Hilbert space). If we compare both expressions we find that the second looks like the result of a limiting process of the first one:
$$\begin{aligned} \sum_k \phi_k^* \psi_k &= \sum_k \frac{\langle\phi|k\rangle}{\sqrt{\Delta k}} \frac{\langle k|\psi\rangle}{\sqrt{\Delta k}} \Delta k \\ &\overset{\Delta k \to 0}{\longrightarrow} \int \phi^*(k)\psi(k)\, dk \end{aligned} \tag{3.39}$$

$$\begin{aligned} \text{with} \qquad \psi(k) &= \langle\tilde{k}|\psi\rangle = \lim_{\Delta k \to 0} \frac{\langle k|\psi\rangle}{\sqrt{\Delta k}} \\ \text{and} \qquad \phi^*(k) &= \langle\phi|\tilde{k}\rangle \\ \hookrightarrow \quad |\tilde{k}\rangle &= \lim_{\Delta k \to 0} \frac{|k\rangle}{\Delta k} \end{aligned} \tag{3.40}$$

i.e. the scalar product (3.39) is the representation of the scalar product $\langle\phi|\psi\rangle$ in a continuous basis $\{|\tilde{k}\rangle\}$.

a) Representation of kets

$$\begin{aligned} |\psi\rangle = \sum_k |k\rangle\langle k|\psi\rangle \quad &\longrightarrow \quad \int |\tilde{k}\rangle\langle\tilde{k}|\psi\rangle\, dk \\ &= \quad \int \psi(k)|\tilde{k}\rangle\, dk \end{aligned} \tag{3.41}$$

$\hookrightarrow$ unity operator

$$\hat{1} = \int |\tilde{k}\rangle\langle\tilde{k}|\, dk \tag{3.42}$$

- $\langle\tilde{k}'|\psi\rangle = \int \langle\tilde{k}'|\tilde{k}\rangle\langle\tilde{k}|\psi\rangle\, dk$
$$\Longrightarrow \quad \langle\tilde{k}'|\tilde{k}\rangle = \delta(k' - k) \tag{3.43}$$
$\longrightarrow$ $\{|\tilde{k}\rangle\}$ are not properly normalized and are not elements of $\mathcal{H}$! Mathematically, this fact causes some trouble. Practically, one can work with these states in a very similar fashion as with elements of $\mathcal{H}$:

discrete representation	continuous representation
$\sum_k \|k\rangle\langle k\| = \hat{1}$	$\int \|k\rangle\langle k\| \, dk = \hat{1}$
$\langle k\|k'\rangle = \delta_{kk'}$	$\langle k\|k'\rangle = \delta(k-k')$ (omit tilde from now on)

There are cases where a basis is partly discrete and partly continuous:

$$\hat{1} = \sum_k |k\rangle\langle k| + \int |k\rangle\langle k| \, dk$$

condensed notation (sometimes used):

$$\begin{aligned} \sum\!\!\!\!\!\!\int |k\rangle\langle k| \, dk &= \hat{1} \\ \langle k|k'\rangle &= \delta(k,k') \end{aligned} \tag{3.44}$$

- scalar product in continuous representation

$$\langle\phi|\psi\rangle = \int dk \; \langle\phi|k\rangle\langle k|\psi\rangle = \int \phi^*(k)\psi(k) \, dk$$

note that $|\phi\rangle, \; |\psi\rangle \; \in \; \mathcal{H}$, but $|k\rangle \; \notin \; \mathcal{H}$!

b) Representation of operators

$$\begin{aligned} \hat{A} \; = \; \hat{1}\hat{A}\hat{1} \; &= \int |k\rangle\langle k|\hat{A}|k'\rangle\langle k'| \, dkdk' \\ &= \int |k\rangle\hat{A}(k,k')\langle k'| \, dkdk' \end{aligned} \tag{3.45}$$

"generalized matrix elements" $A(k,k') = \langle k|\hat{A}|k'\rangle$

- $$\begin{aligned} \langle k|\hat{A}|\psi\rangle &= \int \langle k|\hat{A}|k'\rangle\langle k'|\psi\rangle \, dk' \\ &= \int A(k,k') \; \psi(k') \, dk' \end{aligned} \tag{3.46}$$

- $$\langle\phi|\hat{A}|\psi\rangle = \int \phi^*(k)\hat{A}(k,k')\psi(k') \, dkdk' \tag{3.47}$$

c) Eigenvalue equations

- Discrete spectrum (as before, but this time we'd like to represent the eigenvalue problem with respect to continuous basis)

$$\hat{A}|u_{a_i}\rangle = a_i|u_{a_i}\rangle \ , \quad (|u_{a_i}\rangle \ u_{a_i}\rangle \ \in \ \mathcal{H} \ ; \ \hat{A} = \hat{A}^\dagger)$$

$$\begin{aligned} \hookrightarrow \quad & \int \langle k|\hat{A}|k'\rangle\langle k'|u_{a_i}\rangle \ dk' \ = \ a_i\langle k|u_{a_i}\rangle \\ \Longleftrightarrow \quad & \int A(k,k')u_{a_i}(k') \ dk' \ = \ a_i \ u_{a_i}(k) \end{aligned} \tag{3.48}$$

$\longrightarrow$ eigenvalue problem becomes an integral equation

special case (but important):

$$\begin{aligned} A(k,k') \ = \ & f(k)\delta(k-k') + g(k)\frac{d}{dk}\delta(k-k') \\ & + \ h(k)\frac{d^2}{dk^2}\delta(k-k') \ + \ \ldots \end{aligned} \tag{3.49}$$

$\hookrightarrow$ insertion into (3.48) yields with standard properties of δ-function (and its derivatives)

$$\hookrightarrow \quad \Big(f(k) + g(k)\frac{d}{dk} + h(k)\frac{d^2}{dk^2} + \ldots\Big)u_{a_i}(k) = a_i \ u_{a_i}(k) \tag{3.50}$$

integral eq. reduces to differential eq.

- Continuous spectrum

$$\hat{B}|v_b\rangle \ = \ b|v_b\rangle \tag{3.51}$$

$$\langle v_b|v_{b'}\rangle \ = \ \delta(b-b') \tag{3.52}$$

this problem cannot be treated with mathematical rigor, as $|v_b\rangle \ \notin \ H$ (one cannot even write down eq. (3.51)), but if we stretch the rules somewhat we can describe the continuous spectrum in a formally simple way.

  - as in the case of the discrete spectrum we can prove that $b \ \in \ \mathbb{R}$ if $\hat{B} = \hat{B}^\dagger$
  - $\langle v_{b'}|\hat{B}|v_b\rangle = b\langle v_{b'}|v_b\rangle = b\delta(b-b')$

if $\{|v_b\rangle\}$ is complete we have:

$$\begin{aligned}\hat{B} &= \int |v_b\rangle\langle v_b|\hat{B}|v_{b'}\rangle\langle v_{b'}|\ dbdb' \\ &= \int |v_b\rangle b'\delta(b-b')\langle v_{b'}|\ dbdb' \\ &= \int |v_b\rangle b\langle v_b|\ db \end{aligned} \tag{3.53}$$

(generalized spectral representation)
For an operator with mixed discrete and continuous spectrum we have

$$\begin{aligned}\hat{B} &= \sum_i b_i|b_i\rangle\langle b_i| + \int b|b\rangle\langle b|\ db \\ &\equiv \not{\sum} b|b\rangle\langle b|\ db\end{aligned}$$

(in condensed notation)

- our statements about the eigenvalue problems of commutating operators and about degeneracies translate very directly to the continuous case.

further reading: [Gro]

d) Eigendifferentials (Weyl)

One option to deal with the continuous spectrum in terms of legitimate Hilbert space vectors is the concept of eigendifferentials. They are the formal analogies of wave packets:

$$|v_{b,\Delta b}\rangle \equiv \frac{1}{\sqrt{\Delta b}} \int_b^{b+\Delta b} |\tilde{v}_{b'}\rangle\ db' \tag{3.54}$$

$$\text{with} \qquad |\tilde{v}_{b'}\rangle = \lim_{\Delta b' \to 0} \frac{|v_{b'}\rangle}{\sqrt{\Delta b'}}$$

These kets are normalized properly:

$$\begin{aligned}\langle v_{b,\Delta b}|v_{b,\Delta b}\rangle &= \frac{1}{\Delta b}\int_b^{b+\Delta b} db' \int_b^{b+\Delta b} db'' \underbrace{\langle \tilde{v}_{b'}|\tilde{v}_{b''}\rangle}_{=\delta(b'-b'')} \\ &= \frac{1}{\Delta b}\int_b^{b+\Delta b} db \ = \ 1\end{aligned}$$

Eigendifferentials are approximate eigenvectors in the continuous spectrum.

further reading: (e.g.) [Gre] chap. 5

Literature on the mathematical framework of QM:

a) QM textbooks [Bal], [Gri], [Jel], [Mes] and [Sha]

b) Mathematics for physicists [Arf] and [FK]

c) Mathematical textbooks [Gro] and [Heu]

3.2 From wave mechanics to QM

We'd like to express our wave mechanics of chapter 2 in terms of our new mathematical language. We are thereby led to the conclusion that wave mechanics is nothing else but the representation of a more abstract theory in configuration (sometimes called position) space. We have already seen that we can switch from configuration space to momentum space via Fourier transformation. In our new language this is nothing else but the special case of a unitary change of representation (cf. chapter 3.1.3). Our final goal will be to peel off any representation from quantum theory (cf. chapter 3.3)

But first, let's revisit wave mechanics (in the one-dimensional world)

3.2.1 State

$\longrightarrow$ is characterized by quadratically integrable wave function $\psi(x)$
According to chapter 3.1.6 we can write

$$\psi(x) = \langle x|\psi\rangle \tag{3.55}$$

$\psi(x)$ is the coordinate space (configuration/position space) representation of $|\psi\rangle \in \mathcal{H}$

$$\hookrightarrow \quad \langle\psi|\psi\rangle = \int \langle\psi|x\rangle\langle x|\psi\rangle \, dx = \int |\psi(x)|^2 \, dx = 1$$

with $|\psi(x)|^2 = |\langle x|\psi\rangle|^2$: probability density (cf. chapter 2.3).
Each state vector can be expanded in the continuous basis:

$$|\psi\rangle = \hat{1}|\psi\rangle = \int |x\rangle\psi(x) \, dx \tag{3.56}$$

Momentum space representation (according to eq. (2.64))

$$\begin{aligned} \langle p|\psi\rangle \;=\; \psi(p) \;&=\; \frac{1}{\sqrt{2\pi\hbar}} \int \psi(x) e^{-\frac{i}{\hbar}px} \, dx \\ &=\; \int \frac{e^{-\frac{i}{\hbar}px}}{\sqrt{2\pi\hbar}} \, \langle x|\psi\rangle \, dx \;\stackrel{!}{=}\; \int \langle p|x\rangle\langle x|\psi\rangle \, dx \end{aligned}$$

$\longrightarrow$ identify (unitary) 'transformation matrix'

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{\frac{i}{\hbar}px} \tag{3.57}$$

$$\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-\frac{i}{\hbar}px} \tag{3.58}$$

$\longrightarrow$ transformation between coordinate and momentum spaces is given by plane waves (i.e. Fourier transformation)
interpretation: $\langle x|p\rangle$ is the coordinate space representation of the vector $|p\rangle \notin \mathcal{H}$ etc. What is $|p\rangle$?

3.2.2 Eigenvalue problems etc.

$\hookrightarrow$ $|p\rangle$ is the eigenvector of a hermitian operator $\hat{p}$ with eigenvalue p :

$$\hat{p}|p\rangle = p|p\rangle \ , \quad \hat{p} = \hat{p}^\dagger \tag{3.59}$$

similarly :

$$\hat{x}|x\rangle = x|x\rangle \ , \quad \hat{x} = \hat{x}^\dagger \tag{3.60}$$

"normalization":

$$\langle x|x'\rangle = \int \langle x|p\rangle\langle p|x'\rangle \, dp \overset{(3.57)}{=} \frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar}p(x-x')} \, dp$$

$$= \delta(x-x') \tag{3.61}$$

$$\langle p|p'\rangle = \ldots \overset{(3.58)}{=} \delta(p-p') \tag{3.62}$$

Note that completeness of $\{|x\rangle\}$ and $\{|p\rangle\}$ is a consequence of the Fourier theorem.

- spectral representation (cf. eq. (3.53))

$$\hat{x} = \int |x\rangle x\langle x| \, dx \tag{3.63}$$

$$\hat{p} = \int |p\rangle p\langle p| \, dp \tag{3.64}$$

- change of representation

consider :

$$\langle x'|\hat{p}|x\rangle = \int \langle x'|p'\rangle\langle p'|\hat{p}|p\rangle\langle p|x\rangle \, dpdp'$$

$$= \frac{1}{2\pi\hbar} \int e^{\frac{i}{\hbar}p'x'} p\delta(p'-p) e^{-\frac{i}{\hbar}px} \, dpdp'$$

$$= \frac{1}{2\pi\hbar} \int p e^{\frac{i}{\hbar}p(x'-x)} \, dp$$

$$= -\frac{\hbar}{i} \frac{d}{dx} \delta(x-x')$$

$$\equiv -\frac{\hbar}{i} \frac{d}{dx} \langle x'|x\rangle \tag{3.65}$$

(the last equality can be proven by considering, that $\frac{d}{dx}\langle x'|x\rangle = \frac{d}{dx}\int\langle x'|p\rangle\langle p|x\rangle\ dp$)

from eq. (3.65) it follows, that

$$\begin{aligned} \hat{p}|x\rangle &= -\frac{\hbar}{i}\frac{d}{dx}|x\rangle \\ \hookrightarrow \quad \langle x'|\hat{p}|\psi\rangle &= \int\langle x'|\hat{p}|x\rangle\langle x|\psi\rangle\ dx \\ &\overset{(3.65)}{=} -\frac{\hbar}{i}\int\psi(x)\delta'(x-x')\ dx \\ &= \frac{\hbar}{i}\frac{d}{dx'}\psi(x') \\ &= \hat{p}_{(x')}\psi(x') \end{aligned}$$

$\longrightarrow$ the coordinate space representation of vector $\hat{p}|\psi\rangle$ is given by $\frac{\hbar}{i}d_{x'}\psi(x')$; a result that we know from wave mechanics (write $\hat{p}_{(x')} \equiv \frac{\hbar}{i}d_{x'}$). Similarly one finds: $\langle x'|\hat{x}|\psi\rangle = x'\psi(x')$

3.2.3 Commutators

In coordinate space representation we have

$$\begin{aligned} (\hat{x}\hat{p}_{(x)} - \hat{p}_{(x)}\hat{x})\psi(x) &= \frac{\hbar}{i}(x\ d_x - d_x\ x)\psi(x) \\ &= i\hbar\psi(x) \\ \Longrightarrow \quad [\hat{x}, \hat{p}_{(x)}] &= i\hbar \end{aligned}$$

but this result can be proven to be independent of any representation:

$$\begin{aligned} \hookrightarrow \quad \langle x'|\hat{x}\hat{p} - \hat{p}\hat{x}|\psi\rangle &= \langle x'|\hat{x}\hat{p}|\psi\rangle - \langle x'|\hat{p}\hat{x}|\psi\rangle \\ &\overset{(3.60)}{=} x'\hat{p}_{(x')}\psi(x') - \int\langle x'|\hat{p}|x\rangle\langle x|\hat{x}|\psi\rangle\ dx \\ &\overset{(3.59),(3.65)}{=} x'\hat{p}_{(x')}\psi(x') - \frac{\hbar}{i}\frac{d}{dx'}(x'\psi(x')) \\ = \quad \ldots \quad &= i\hbar\psi(x') \\ &= i\hbar\langle x'|\psi\rangle \end{aligned}$$

extract:

$$[\hat{x}, \hat{p}] = i\hbar \tag{3.66}$$

Interestingly, one can change the line of argumentation and can postulate the fundamental commutator eq. (3.66) for hermitian operators $\hat{x},\ \hat{p}$.

Without any further physical ingredients one can prove the following

- $\hat{x},\ \hat{p}$ have continuous spectra (eq. (3.63), (3.64))
- $|x\rangle,\ |p\rangle$ are normalized with respect to δ-functions (eq. (3.61), (3.62))
- coordinate space representation of $\hat{p}|\psi\rangle$
- momentum space representation of $\hat{x}|\psi\rangle$
- plane waves form the unitary transformation (eq. (3.57), (3.58))
- stationary Schrödinger equation
- uncertainty relation

see, e.g. [Mes] QM I, chap. 8.1; [Fic], chap. 4.1

Let's consider the 6^{th} item on the list

3.2.4 Stationary Schrödinger equation

From the time-dependent Schrödinger equation (SE) we derived eq. (2.86), the stationary SE

$$\Big(-\frac{\hbar^2}{2m}d_x^2 + V(x)\Big)\psi(x) = E\psi(x) \tag{3.67}$$

Let's show, that eq. (3.67) is identical to the coordinate space representation of the abstract eigenvalue problem

$$\boxed{\hat{H}|\psi\rangle = E|\psi\rangle} \tag{3.68}$$

with $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$ (we assume $\hat{V} = V(\hat{x})$ and $\hat{H} = \hat{H}^\dagger$)

$$\begin{aligned}
\underline{\text{proof :}} \qquad \langle x|\hat{H}|\psi\rangle &= \langle x|\frac{\hat{p}^2}{2m} + V(\hat{x})|\psi\rangle \\
&= \frac{1}{2m}\int \langle x|\hat{p}^2|x'\rangle\psi(x')\ dx' + \int \langle x|V(\hat{x})|x'\rangle\psi(x')\ dx' \\
\text{(cf. eq. (3.49, 3.50))}^1 &= -\frac{\hbar^2}{2m}\int \delta''(x-x')\psi(x')\ dx' + \int V(x')\delta(x-x')\psi(x')\ dx'
\end{aligned}$$

[1] similarly to eq. (3.65) one finds

$$\begin{aligned}
\langle x|\hat{p}^2|x'\rangle &= \frac{1}{2\pi\hbar}\int p^2 e^{\frac{i}{\hbar}p(x-x')}\ dp \ = \ -\hbar^2\delta''(x-x') \\
\text{and} \qquad \hat{p}^2|x'\rangle &= -\hbar^2\ d_{x'}^2|x'\rangle
\end{aligned}$$

$$= \Big(-\frac{\hbar^2}{2m}\, d_x^2 + V(x) \Big) \psi(x)$$

$$\overset{\text{rhs}}{=} E\langle x|\psi\rangle = E\psi(x) \qquad \text{q.e.d.}$$

In chapter 2.4 we learned that the eigenvalues E of eq. (3.67) (or eq. (3.68)) are the possible energies that one can measure[2]. In the next section, we will elevate this statement to a postulate for all hermitian operators!

- SE in momentum space

  starting point: abstract eigenvalue eq. (3.68):

$$\begin{aligned} \lhd \qquad \langle p|\hat{H}|\psi\rangle &= E\langle p|\psi\rangle \\ \text{lhs}: \qquad &= \int \langle p| \frac{\hat{p}^2}{2m} + \hat{V}|p'\rangle \psi(p')\, dp' \\ &= \frac{1}{2m} \int p'^2 \delta(p-p')\psi(p')\, dp' + \int \langle p|V|p'\rangle \psi(p')\, dp' \end{aligned}$$

$$\boxed{\iff \quad \frac{p^2}{2m}\psi(p) + \int V(p,p')\psi(p')\, dp' = E\psi(p) \qquad (3.69)}$$

  SE in momentum space is not a differential but an integral equation (in general more difficult to solve)

  if $\hat{V} = V(\hat{x})$:

$$\begin{aligned} V(p,p') \equiv \langle p|V|p'\rangle &= \int \langle p|x\rangle V(x) \langle x|p'\rangle\, dx \\ &= \frac{1}{2\pi\hbar} \int V(x) e^{\frac{i}{\hbar}(p-p')x}\, dx \qquad \text{(Fourier integral)} \end{aligned}$$

  (This expression plays an important role in scattering theory when one considers elastic scattering, e.g., from a Coulomb potential, which leads to Rutherford's cross section formula; cf. [LL], § 137)

- Question: What about the time-dependent SE?

  $\longrightarrow$ this eq. cannot be derived form commutators etc., but has to be postulated as an independent axiom of QM (see next section)

[2] and that, in general, the spectrum of $\hat{H}$ may be (at least partly) discrete (i.e. energy levels are quantized).

3.3 The postulates of Quantum Mechanics

We'd like to summarize the fundamental statements (that we have already encountered) as 6 postulates:

3.3.1 States

are characterized by kets $|\psi\rangle \in \mathcal{H}$.
(cf. chapter 3.1.1: this is motivated by the principle of superposition)

3.3.2 Observables

Observables are characterized by linear, hermitian operators. Their (real) eigenvalues are the possible outcomes of measurements (spectra can be (partially) discrete or continuous)

Often, one calls hermitian operators with a complete set of eigenvectors 'observables'. We will consider only such (hermitian) operators

$$\hookrightarrow \quad \hat{A} = \sum_n a_n \hat{P}_n$$

(spectral representation, eq. (3.32))

3.3.3 Expectation values

(of observables) (cf. chapter 2.3.4)

$$\text{define :} \qquad \langle A \rangle := \frac{\langle \psi | \hat{A} | \psi \rangle}{\langle \psi | \psi \rangle} \qquad \in \mathbb{R} \tag{3.70}$$

if state is normalized, i.e., $\langle \psi | \psi \rangle = 1$ we can write, e.g.

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \int \langle \psi | x \rangle \langle x | \hat{A} | x' \rangle \langle x' | \psi \rangle \; dx dx'$$

(for a one-dimensional system)

$$\text{if} \qquad \hat{A} = A(\hat{x}) \quad \hookrightarrow \quad \langle x | \hat{A} | x' \rangle = A(x') \delta(x - x')$$

$$\begin{aligned} \hookrightarrow \quad \langle A \rangle &= \int \psi^*(x) A(x) \psi(x) \; dx \\ &= \int A(x) |\psi(x)|^2 \; dx \end{aligned} \tag{3.71}$$

(cf. eq. (2.71) for a 3-dimensional system)

- For N particles we have

$$\hat{1} = \int |\mathbf{r}_1 ... \mathbf{r}_N\rangle\langle \mathbf{r}_1 ... \mathbf{r}_N| \; d^3r_1 ... d^3r_N \tag{3.72}$$

and for $\hat{A} = A(\hat{\mathbf{r}}_1 ... \hat{\mathbf{r}}_N)$ we obtain similarly to eq. (3.71)

$$\begin{aligned} \langle A \rangle &= \int \Psi^*(\mathbf{r}_1 ... \mathbf{r}_N) A(\mathbf{r}_1 ... \mathbf{r}_N) \Psi(\mathbf{r}_1 ... \mathbf{r}_N) \; d^3r_1 ... d^3r_N \\ &= \int A(\mathbf{r}_1 ... \mathbf{r}_N) |\Psi(\mathbf{r}_1 ... \mathbf{r}_N)|^2 \; d^3r_1 ... d^3r_N \end{aligned} \tag{3.73}$$

- For $\hat{A} \equiv \hat{\mathbf{p}}$ we obtain (for <u>one</u> particle again to facilitate the notation)

$$\begin{aligned} \langle \mathbf{p} \rangle &= \int \langle \psi | \mathbf{p} \rangle \langle \mathbf{p} | \hat{\mathbf{p}} | \mathbf{p}' \rangle \langle \mathbf{p}' | \psi \rangle \; d^3p d^3p' \\ &= \int \psi^*(\mathbf{p}) \mathbf{p} \psi(\mathbf{p}) \qquad \text{(this is eq. (2.72))} \\ &\overset{\text{or:}}{=} \int \langle \psi | \mathbf{r} \rangle \langle \mathbf{r} | \hat{\mathbf{p}} | \mathbf{r}' \rangle \langle \mathbf{r}' | \psi \rangle \; d^3r d^3r' \\ &\overset{\text{cf. eq. (3.65)}}{=} -\frac{\hbar}{i} \int \psi^*(\mathbf{r}) \Big(\int \boldsymbol{\nabla}_{\mathbf{r}'} \delta(\mathbf{r}' - \mathbf{r}) \psi(\mathbf{r}') \; d^3r' \Big) \; d^3r \\ &= \int \psi^*(\mathbf{r}) \frac{\hbar}{i} \boldsymbol{\nabla} \psi(\mathbf{r}) \; d^3r \qquad \text{(this is eq. (2.76))} \end{aligned} \tag{3.74, 3.75}$$

In the same fashion we can re-derive eq. (2.78) etc.

- With respect to $\hat{A}$'s eigenbasis we have

$$\langle A \rangle = \sum_n a_n |\langle a_n | \psi \rangle|^2 \; , \quad \text{(compare to eqs. (2.68), (2.72))} \tag{3.76}$$

(follows from spectral representation of $\hat{A}$)

interpretation: a_n are the possible outcomes of measurements (postulate 3.3.2), and $\omega_n = |\langle a_n | \psi \rangle|^2 \in \mathbb{R}$ are the corresponding probabilities

Note that $\omega_n = \langle \psi | a_n \rangle \langle a_n | \psi \rangle = \langle \psi | \hat{P}_n | \psi \rangle = \langle P_n \rangle$

one calls $\langle a_n | \psi \rangle \in \mathbb{C}$ 'probability amplitudes'

$$\text{if} \qquad |\psi\rangle \equiv |a_m\rangle \quad \hookrightarrow \quad \langle A \rangle = a_m \; , \quad \omega_m = 1$$

this is a certain measurement.

In this case one can show that

$$(\Delta A)^2 := \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2 = 0$$

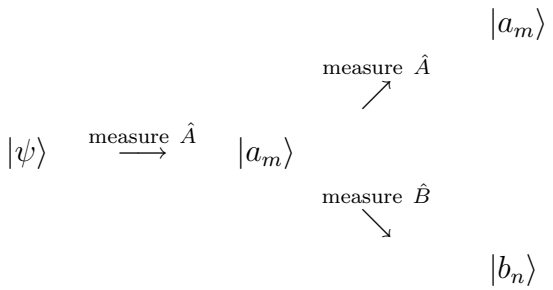
and vice versa (which is quite evident)
(for details see [Blöc], chap. 7.2)

3.3.4 Measurements

We cannot delve into the conceptual difficulties of this issue (which is controversial to the present day). For laboratory measurements the 'Kopenhagen interpretation' has been and still is successful in (almost) all cases, although its foundations are still under discussion.

Literature: [Aud] and [Omnb]
More technical accounts: [d'E] and [Omna]

From postulates 3.3.1 - 3.3.3 we know the following



The measurement of $\hat{A}$ changes (disturbs) the state $|\psi\rangle$. After the measurement the system is characterized by the eigenstate $|a_m\rangle$. If we measure $\hat{A}$ again we re-obtain a_m because this is then a certain measurement. If we measure $\hat{B}$ we disturb the system again (in general) and change the state to one of $\hat{B}$'s eigenstates. One calls these 'perturbations' or changes

"reduction (collapse) of the wave function".

There is no element in the theory that tells us which eigenvector is chosen, we can only calculate (know) the corresponding probability; the collapse itself is 'indeterministic' (which many physicists find unsatisfactory)

We can think of a measurement as a projection onto the corresponding eigenstate and re-normalization of the state because after the measurement the system is in the eigenstate with probability one!

3.3.5 Commutation relations

As mentioned in chapter 3.2.3 we postulate fundamental commutation relations (which cannot be derived, but which rest on plausibility arguments and correspondence rules)

a) Important commutation relations

1) The fundamental commutator for one particle in one dimension is eq. (3.66)

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

2) One (spinless) particle in three dimensions

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij} \tag{3.77}$$
$$[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = 0 \tag{3.78}$$

3) We can then consider operator functions $\hat{F} = F(\hat{x}_i, \hat{p}_j)$

one can show : $$[\hat{F}, \hat{p}_j] = i\hbar\frac{\partial \hat{F}}{\partial \hat{x}_j} \tag{3.79}$$

(using eq. (3.77), (3.78))

proof : see [Blöc] $$[\hat{F}, \hat{x}_j] = \frac{\hbar}{i}\frac{\partial \hat{F}}{\partial \hat{p}_j} \tag{3.80}$$

4) Example for an operator function:
angular momentum operator defined by

$$\hat{\mathbf{l}} := \hat{\mathbf{r}} \times \hat{\mathbf{p}} \tag{3.81}$$

$(\hat{l}_i = \hat{l}_i^{\dagger}\ , \quad i = 1, 2, 3)$

we can calculate various commutators on the basis of eq. (3.79) and (3.80), e.g.

$$[\hat{l}_3, \hat{x}_3] = [\hat{l}_3, \hat{p}_3] = 0$$
$$[\hat{l}_3, \hat{x}_1] = i\hbar\hat{x}_2$$
$$[\hat{l}_3, \hat{p}_1] = i\hbar\hat{p}_2$$

and

$$[\hat{l}_i, \hat{l}_j] = i\hbar \sum_{k=1}^{3} \varepsilon_{ijk} \hat{l}_k \tag{3.82}$$

$$\text{with} \quad \varepsilon_{ijk} = \begin{cases} 1 & \text{cyclic permutation } (ijk) \\ -1 & \text{anticyclic permutation } (ijk) \\ 0 & \text{two like indices } (ijk) \end{cases}$$

and

$$[\hat{\mathbf{l}}^2, \hat{l}_i] = 0$$

The commutators (3.82) are the basis of angular momentum algebra and can be used as definition of angular momentum in QM (see chapter 4.3).

5) (electron) spin (chapter 4.4.4)

$\longrightarrow$ define operator $\hat{\mathbf{s}} = (\hat{s}_1, \hat{s}_2, \hat{s}_3)\ , \quad \hat{s}_i = \hat{s}_i^\dagger \quad \forall\ i$

and require $[\hat{s}_i, \hat{s}_j] = i\hbar \sum_k \varepsilon_{ijk} \hat{s}_k$

and $[\hat{s}_i, \hat{x}_j] = [\hat{s}_i, \hat{p}_j] = 0\ , \quad \forall\ i, j$

together with eq. (3.77) and eq. (3.78) these relations form the basis for the discussion of a one-particle system with spin.

b) General uncertainty relation

The commutator relations are intimately related to the (general) uncertainty relation(s). For hermitian operators we prove

$$\Delta A\ \Delta B \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle| \tag{3.83}$$

"two non-commuting observables cannot be measured simultaneously with arbitrary accuracy."

proof: the 'square variations' are defined by

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle\ , \quad (\Delta B)^2 = \langle (B - \langle B \rangle)^2 \rangle$$

in addition, we define (hermitian) operators

$$\begin{aligned} \hat{a} &:= \hat{A} - \langle A \rangle \hat{1} \\ \hat{b} &:= \hat{B} - \langle B \rangle \hat{1} \end{aligned}$$

and consider

$$\begin{aligned}(\Delta A)^2(\Delta B)^2 &= \langle\psi|\hat{a}^2|\psi\rangle\langle\psi|\hat{b}^2|\psi\rangle \\ &= \langle\hat{a}\psi|\hat{a}\psi\rangle\langle\hat{b}\psi|\hat{b}\psi\rangle \\ &\geq |\langle\hat{a}\psi|\hat{b}\psi\rangle|^2 \qquad \text{Schwarz inequality, chapter 3.1.1} \\ &= |\langle\psi|\hat{a}\hat{b}|\psi\rangle|^2\end{aligned}$$

$$\lhd \qquad \hat{a}\hat{b} = \underbrace{\frac{\hat{a}\hat{b}+\hat{b}\hat{a}}{2}}_{\text{hermitian}} + i\underbrace{\frac{\hat{a}\hat{b}-\hat{b}\hat{a}}{2i}}_{\text{hermitian}}$$

$$\hookrightarrow \quad \langle\psi|\hat{a}\hat{b}|\psi\rangle = \underbrace{\langle\psi|\frac{\hat{a}\hat{b}+\hat{b}\hat{a}}{2}|\psi\rangle}_{\in\,\mathbb{R}} + i\underbrace{\langle\psi|\frac{\hat{a}\hat{b}-\hat{b}\hat{a}}{2i}|\psi\rangle}_{\in\,\mathbb{R}}$$

$$\begin{aligned}\hookrightarrow \quad |\langle\psi|\hat{a}\hat{b}|\psi\rangle|^2 &= \Big(\langle\psi|\frac{\hat{a}\hat{b}+\hat{b}\hat{a}}{2}|\psi\rangle\Big)^2 + \Big(\langle\psi|\frac{\hat{a}\hat{b}-\hat{b}\hat{a}}{2i}|\psi\rangle\Big)^2 \\ &\geq \Big(\langle\psi|\frac{\hat{a}\hat{b}-\hat{b}\hat{a}}{2i}|\psi\rangle\Big)^2 \\ &= \frac{1}{4}|\langle\psi|[\hat{a},\hat{b}]|\psi\rangle|\end{aligned}$$

it is straightforward to show that $[\hat{a},\hat{b}] = [\hat{A},\hat{B}] \;\hookrightarrow$ q.e.d.

Comments:

1. $\exists\, |\psi\rangle \in \mathcal{H}: \quad \Delta A\Delta B = \frac{1}{2}|\langle[\hat{A},\hat{B}]\rangle|$ (minimal uncertainty)
   In this case it follows from Schwarz's (in-)equality that

$$\hat{a}|\psi\rangle = c\hat{b}|\psi\rangle\,, \qquad (c \in \mathbb{C})$$

   additionally, we require

$$\begin{aligned}\langle\psi|\hat{a}\hat{b}+\hat{b}\hat{a}|\psi\rangle &= 0 \\ \iff \quad c^*\langle\psi|\hat{b}^2|\psi\rangle + c\langle\psi|\hat{b}^2|\psi\rangle &= 0 \\ \iff \quad \Re\, c\Big(\langle\psi|\hat{b}^2|\psi\rangle\Big) &= 0\end{aligned}$$

   $\Longrightarrow$ c is imaginary!

   note that

$$\langle\psi|\hat{b}^2|\psi\rangle = 0 \iff \hat{B}|\psi\rangle = \langle B\rangle|\psi\rangle$$

   in this case we have $\Delta B = \Delta A\Delta B = 0$ (certain measurement)

2. $[\hat{x}, \hat{p}] = i\hbar$

$$\boxed{\implies \quad \Delta p \Delta x \geq \frac{\hbar}{2}} \tag{3.84}$$

3. $[\hat{l}_x, \hat{l}_y] = i\hbar \hat{l}_z$

$$\implies \quad \Delta l_x \Delta l_y \geq \frac{\hbar}{2} |\langle l_z \rangle| \tag{3.85}$$

4. in general: Two Operators $\hat{A},\ \hat{B}$ are called 'complementary' operators:

$$\iff \quad [\hat{A}, \hat{B}] \neq 0$$

$\overset{3.83}{\implies}$ they cannot be measured simultaneously with certainty! What can we say about measurements of complementary operators: (cf. page 67)

state	$\lvert\psi\rangle$	$\xrightarrow{\hat{A}}$	$\lvert a_m\rangle$	$\xrightarrow{\hat{B}}$	$\lvert b_n\rangle$	$\xrightarrow{\hat{A}}$	$\lvert a_k\rangle$
measured value			a_m		b_n		a_k
probability			$\lvert\langle a_m \lvert\psi\rangle\rvert^2$		$\lvert\langle a_m \lvert b_n\rangle\rvert^2$		$\lvert\langle a_k \lvert b_n\rangle\rvert^2$

$\longrightarrow$ measurement of $\hat{A}$ is not necessarily reproduced!

5. Two operators $\hat{A},\ \hat{B}$ are called 'compatible' operators:

   $\iff \quad [\hat{A}, \hat{B}] = 0 \quad \iff$ common set of eigenvectors (cf. chapter 3.1.5)

   measurements:

   (a) no degeneracy

state	$\lvert\psi\rangle$	$\xrightarrow{\hat{A}}$	$\lvert a_m\rangle$	$\xrightarrow{\hat{B}}$	$\lvert a_m\rangle$	$\xrightarrow{\hat{A}}$	$\lvert a_m\rangle$
measured value			a_m		b_m		a_m
probability			$\lvert\langle a_m \lvert\psi\rangle\rvert^2$		1		1
					$\uparrow$		$\uparrow$

these are certain measurements as state is an eigenstate

   (b) degeneracy (of $\hat{A}$)

state	$\lvert\psi\rangle$	$\xrightarrow{\hat{A}}$	$\left\{\lvert a_m^\mu\rangle,\ \mu = 1, ...\right\}$	$\xrightarrow{\hat{B}}$	$\lvert a_m^\mu\rangle$	$\xrightarrow{\hat{A}}$	$\lvert a_m^\mu\rangle$
			i.e.[3] $\lvert\psi'\rangle = \sum_\mu c_\mu^m \lvert a_m^\mu\rangle$				
measured value			a_m		b_m^μ		a_m
probability			$\sum_\mu \lvert\langle a_m^\mu \lvert\psi\rangle\rvert^2$		$\lvert\langle a_m^\mu \lvert\psi'\rangle\rvert^2 = \lvert c_m^\mu\rvert^2$		1

This scheme leads us to

6. Complete set of compatible observables

   $\longrightarrow$ measure compatible operators (with degenerate spectra) until the dimension of their simultaneous eigenspace is 1 $\hookrightarrow$ in this case the state of the system is completely determined

$$|\psi\rangle \;=\; |abc...\rangle$$

$\llcorner$ "quantum numbers" (i.e. eigenvalues of complete set of observables characterize state)

$$\hookrightarrow \quad \sum\!\!\!\!\!\!\int_{abc...} |abc...\rangle\langle abc...| = \hat{1}$$

   The number of operators which are needed to determine the state of the system completely is related to the degrees of freedom of the system.

   e.g. - one particle in one dimension: one observable ($\hat{x}$ or $\hat{p}$) suffices to determine the state
   - one particle in three dimensions: need three compatible observables (e.g. $\hat{x}_1, \hat{x}_2, \hat{x}_3$; or (see later) $\hat{H}, \hat{\mathbf{l}}^2, \hat{l}_z$)

7. What about the energy-time uncertainty relation?

$$\Delta\tau \; \Delta E \geq \frac{\hbar}{2} \tag{3.86}$$

   $\longrightarrow$ it does not follow from a commutator via eq. (3.83) because there is no time operator in (textbook) QM
   $\longrightarrow$ eq. (3.86) has to be derived and interpreted differently (see chapter 3.4)

---

[3] c_m^μ can be determined in the following way:

$$\begin{aligned} |\psi'\rangle &= C\sum_\mu |a_m^\mu\rangle\langle a_m^\mu|\psi\rangle \\ \langle\psi'|\psi'\rangle &= 1 = C^2\sum_\mu |\langle a_m^\mu|\psi\rangle|^2 \\ \hookrightarrow \quad c_m^\mu &\equiv C\langle a_m^\mu|\psi\rangle = \frac{\langle a_m^\mu|\psi\rangle}{\sqrt{\sum|\langle a_m^\mu|\psi\rangle|^2}} \end{aligned}$$

3.3.6 Dynamics

The last postulate which completes the formal scheme of QM is about the time development of quantum systems.

We postulate that the dynamics is governed by the time-dependent Schrödinger equation

$$\begin{aligned} i\hbar d_t|\psi(t)\rangle &= \hat{H}|\psi(t)\rangle \\ |\psi(t_0)\rangle &= |\psi_0\rangle \end{aligned} \tag{3.87}$$

($\hat{H}$ may or may not depend on time)

The time t in this equation is the 'usual' classical time, i.e., it is what we measure with a classical clock; it is not an observable of the quantum system!

Note that eq. (3.87) boils down to eq. (2.40) or eq. (2.42) in coordinate space.

in one dimension:

$$\begin{aligned} i\hbar\langle x|d_t\psi(t)\rangle &= i\hbar d_t\langle x|\psi(t)\rangle \\ &= i\hbar\partial_t\psi(x,t) \\ &= \langle x|\hat{H}|\psi(t)\rangle \\ &\overset{\text{p. 63}}{=} \Big(-\frac{\hbar^2}{2m}d_x^2 + V(x)\Big)\psi(x,t) \end{aligned}$$

in momentum space we have: (cf. eq. (3.69))

$$\begin{aligned} i\hbar\langle p|d_t\psi(t)\rangle &= i\hbar\partial_t\psi(p,t) \\ &= \langle p|\hat{H}|\psi(t)\rangle \\ &= \frac{p^2}{2m}\psi(p,t) + \int V(p,p')\psi(p',t)\ dp' \end{aligned}$$

3.4 Equations of motion

We elaborate on the last topic: the time-development of quantum systems. The time-dependent Schrödinger equation (TDSE) is an initial value problem and is linear, i.e.

$$|\psi(t_0)\rangle \overset{\text{TDSE}}{\longrightarrow} |\psi(t)\rangle$$

Let's characterize this linear map.

3.4.1 Time-development (evolution) operator

Define $\hat{U}(t, t_0)$ via

$$|\psi(t)\rangle = \hat{U}(t, t_0)|\psi(t_0)\rangle \tag{3.88}$$

due to $|\psi(t_0)\rangle = \hat{U}(t_0, t_0)|\psi(t_0)\rangle$, it follows, that

$$\hat{U}(t_0, t_0) = \hat{1} \tag{3.89}$$

a) Differential equation

TDSE eq. (3.87):

$$\begin{aligned} i\hbar d_t|\psi(t)\rangle &\overset{(3.88)}{=} i\hbar\Big(\frac{d}{dt}\hat{U}(t, t_0)\Big)|\psi(t_0)\rangle \\ &= \hat{H}(t)\hat{U}(t, t_0)|\psi(t_0)\rangle \end{aligned}$$

$$\begin{aligned} \hookrightarrow \quad i\hbar d_t\hat{U}(t, t_0) &= \hat{H}(t)\hat{U}(t, t_0) \\ \hat{U}(t_0, t_0) &= \hat{1} \end{aligned} \tag{3.90}$$

$\longrightarrow$ equivalent with TDSE!

b) Equivalent integral equation

$$\hat{U}(t, t_0) = \hat{1} - \frac{i}{\hbar}\int_{t_0}^{t} \hat{H}(t')\hat{U}(t', t_0)\, dt' \tag{3.91}$$

c) Some properties (without proofs)

(i) $$\hat{U}(t, t') = \hat{U}(t, t'')\hat{U}(t'', t') \tag{3.92}$$
(group property)

(ii) $$\hat{U}^\dagger(t, t_0) = \hat{U}^{-1}(t, t_0) = \hat{U}(t_0, t) \tag{3.93}$$
i.e. $\hat{U}$ unitary $\iff$ $\hat{H}$ hermitian

$$\begin{aligned} \hookrightarrow \quad \langle\psi(t)|\psi(t)\rangle &= \langle\psi(t_0)|\hat{U}^\dagger(t, t_0)\hat{U}(t, t_0)|\psi(t_0)\rangle \\ &= \langle\psi(t_0)|\psi(t_0)\rangle \end{aligned}$$

$\longrightarrow$ norm conservation (cf. chapter 2.3.2)

(iii) For stationary systems ($\partial_t\hat{H} = 0$)

$$\hookrightarrow \quad \hat{U}(t, t_0) = \exp\Big[-\frac{i}{\hbar}\hat{H}(t - t_0)\Big] \tag{3.94}$$

(check it by applying eq. (3.90))

in this case

$$\hookrightarrow \quad |\psi(t)\rangle = \exp\Big[-\frac{i}{\hbar}\hat{H}(t-t_0)\Big]|\psi(t_0)\rangle$$

$$\begin{aligned} \text{if} \qquad \hat{H}|\psi(t_0)\rangle &= E|\psi(t_0)\rangle \\ \text{i.e.} \qquad |\psi(t_0)\rangle &\equiv |\psi_E(t_0)\rangle \qquad \text{(eigenvector of } \hat{H}\text{)} \\ \hookrightarrow |\psi_E(t)\rangle &= e^{-\frac{i}{\hbar}E(t-t_0)}|\psi_E(t_0)\rangle \end{aligned} \tag{3.95}$$

$$|\psi_E(\mathbf{r},t)|^2 \;=\; |\langle\mathbf{r}|\psi_E(t)\rangle|^2 \;=\; |\langle\mathbf{r}|\psi_E(t_0)\rangle|^2 \;=\; |\psi_E(\mathbf{r},t_0)|^2$$

$\longrightarrow$ no change in probability density (stationary state)

This scheme, together with the postulates of the the last chapter, are summarized as formulation of QM in the so-called

"Schrödinger picture"

characteristics:
- states obey TDSE
- observables can depend on time only explicitly ($d_t\hat{A} = \partial_t\hat{A}$); e.g. time-dependent EM field

Since unitary transformations do not change scalar products and eigenvalue spectra, they do not change the physical contents. Hence, we can apply a (time-dependent) unitary transformation to the states and operators of the Schrödinger picture in order to formulate QM in a different 'picture'!

3.4.2 Heisenberg picture

- define Heisenberg state $|\psi_H\rangle$ via

$$\begin{aligned} |\psi_H\rangle &= \hat{U}^\dagger(t,t_0)|\psi_S(t)\rangle \qquad (3.96) \\ &\qquad\qquad \llcorner\ \text{'Schrödinger state' that} \\ &\qquad\qquad\quad \text{fulfills TDSE eq.(3.87)} \\ &= \hat{U}(t_0,t)|\psi_S(t)\rangle \;=\; |\psi_S(t_0)\rangle \\ \Longrightarrow \quad d_t|\psi_H\rangle &= 0 \qquad (3.97) \end{aligned}$$

- transformation of operators (cf. eq. (3.23))

$$\hat{A}_H(t) = \hat{U}^\dagger(t,t_0)\hat{A}_S(t)\hat{U}(t,t_0) \tag{3.98}$$

Consequence:

$$\begin{aligned}\langle A\rangle &= \langle\psi_S(t)|\hat{A}_S(t)|\psi_S(t)\rangle \overset{\text{use inverse transform.}}{=} \\ &= \langle\psi_H|\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0)\hat{A}_H(t)\hat{U}^\dagger(t,t_0)\hat{U}(t,t_0)|\psi_H\rangle \\ &= \langle\psi_H|\hat{A}_H(t)|\psi_H\rangle \end{aligned} \tag{3.99}$$

$\longrightarrow$ invariant as required!

a) Equation of motion

$$\begin{aligned}\lhd \qquad i\hbar d_t\hat{A}_H(t) &= i\hbar d_t\Big\{\hat{U}^\dagger(t,t_0)\hat{A}_S(t)\hat{U}(t,t_0)\Big\} \\ &\overset{(3.90)}{=} -\hat{U}^\dagger(t,t_0)\hat{H}_S(t)\hat{A}_S(t)\hat{U}(t,t_0) \\ &\quad +\hat{U}^\dagger(t,t_0)\hat{A}_S(t)\hat{H}_S(t)\hat{U}(t,t_0) \\ &\quad +i\hbar\hat{U}^\dagger(t,t_0)\big(\partial_t\hat{A}_S\big)\hat{U}(t,t_0) \\ &= \hat{U}^\dagger(t,t_0)\Big\{[\hat{A}_S(t),\hat{H}_S(t)]+i\hbar\partial_t\hat{A}_S\Big\}\hat{U}(t,t_0) \\ &\overset{(3.98)}{=} [\hat{A}_H(t),\hat{H}_H(t)]+i\hbar\partial_t\hat{A}_H\end{aligned}$$

(where we have defined $\partial_t\hat{A}_H = \hat{U}^\dagger(t,t_0)\partial_t\hat{A}_S\hat{U}(t,t_0)$)
Note that commutators are invariant under transformation[4]
$\longrightarrow$ "Heisenberg equation"

$$\begin{aligned} i\hbar\frac{d}{dt}\hat{A}_H(t) &= [\hat{A}_H(t),\hat{H}_H(t)]+i\hbar\partial_t\hat{A}_H(t) \\ \text{initial condition :}\quad \hat{A}_H(t_0) &= \hat{A}_S(t_0)\end{aligned} \tag{3.100}$$

characteristics of Heisenberg picture:
- states are time-independent
- operators obey Heisenberg eq.

b) Eigenvalue problem

$$\begin{aligned}\text{Schrödinger picture :}\qquad \hat{A}_S|a_i^S\rangle &= a_i|a_i^S\rangle \\ \text{Heisenberg picture :}\qquad |a_i^H(t)\rangle &= \hat{U}^\dagger(t,t_0)|a_i^S\rangle \\ \hookrightarrow\quad \hat{A}_H(t)|a_i^H(t)\rangle &= \hat{U}^\dagger(t,t_0)\hat{A}_S|a_i^S\rangle \\ &= a_i|a_i^H(t)\rangle\end{aligned}$$

[4]

$$\begin{aligned}[\hat{A}_S,\hat{B}_S]=0 &\iff [\hat{A}_H,\hat{B}_H]=0 \\ [A_S,B_S]=\hat{C}_S &\iff [A_H,B_H]=\hat{C}_H\end{aligned}$$

$\longrightarrow$ same eigenvalues a_i as required!

c) Transition probabilities

$$\omega_i = |\langle a_i^S|\psi_S(t)\rangle|^2 = |\langle a_i^H(t)|\psi_H\rangle|^2 \qquad \text{(invariant!)}$$

d) Analogy with classical mechanics

- Schrödinger picture is advantageous for practical calculations
- Heisenberg picture is advantageous for formal development; e.g. it shows nicely the formal correspondence between QM and classical mechanics

$$\lhd \qquad i\hbar d_t \hat{x}_j^H \overset{(3.100)}{=} [\hat{x}_j^H, \hat{H}_H] = i\hbar \frac{\partial \hat{H}_H}{\partial \hat{p}_j^H}, \quad (j = 1,2,3)$$

We obtain a similar eq. for the momentum operator

Summary:

$$\begin{aligned} d_t \hat{x}_j^H &= \frac{\partial \hat{H}_H}{\partial \hat{p}_j^H} \qquad (3.101)\\ &\qquad\qquad \text{(correspond to Hamilton eqs.}\\ &\qquad\qquad \text{of classical mechanics)}\\ d_t \hat{p}_j^H &= -\frac{\partial \hat{H}_H}{\partial \hat{x}_j^H} \end{aligned}$$

note that there is a further correspondence: if one introduces 'Poisson brackets' $\{f, g\}$ in classical mechanics

$$\{f, g\} := \sum_i \Big(\frac{\partial f}{\partial x_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial x_i} \Big)$$

classical eq. of motions take the form

$$\frac{d}{dt} A_{\mathrm{kl}}(x_1 ... x_N; p_1 ... p_N; t) = \{A_{\mathrm{kl}}, H_{\mathrm{kl}}\} + \frac{\partial A_{\mathrm{kl}}}{\partial t}\ , \qquad \text{(cf. eq. (3.100))}$$

moreover :

$$\begin{aligned} \{x_i, x_j\} &= \{p_i, p_j\} = 0\\ \{x_i, p_j\} &= \delta_{ij} \end{aligned}$$

$\longrightarrow$ extract correspondence rule (first observed by Dirac) for the transition from classical to quantum mechanics

$$\begin{aligned} \{A_{kl}, B_{kl}\} &\longrightarrow \frac{1}{i\hbar}[\hat{A}, \hat{B}]\\ \text{e.g.} \qquad \{x_i, p_j\} &\longrightarrow \frac{1}{i\hbar}[\hat{x}_i, \hat{p}_j] \end{aligned}$$

("canonical quantization")

e) Constants of motion

defined by $d_t\hat{A}_H(t) = 0$
if $\partial_t\hat{A} = 0$ (which is often the case)

$$\begin{aligned} d_t\hat{A}_H = 0 &\iff [\hat{A}_H, \hat{H}_H] = 0 \\ &\iff [\hat{A}_S, \hat{H}_S] = 0 \end{aligned} \tag{3.102}$$

'constants of motion commute with the Hamiltonian'

in this case : $\hat{A}|a_i\rangle = a_i|a_i\rangle$
$\llcorner$ "good quantum number"
(i.e. 'certain measurement')

Examples:

(i) $\hat{H} = \frac{\hat{p}^2}{2m}$ (free particle)

$$[\hat{p}, \hat{H}] = 0 \longrightarrow \text{momentum conservation}$$

but :

(ii) $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$

$$[\hat{p}, \hat{H}] = [\hat{p}, V(\hat{x})] \overset{(3.80)}{=} \frac{\hbar}{i}\frac{\partial \hat{V}}{\partial \hat{x}} \neq 0$$

f) Expectation values and Ehrenfest's theorems

Let's consider eq. of motion for expectation values (can also be derived in Schrödinger picture)

$$\begin{aligned} \frac{d}{dt}\langle A\rangle &= \langle\psi_H|d_t\hat{A}_H|\psi_H\rangle \\ &\overset{(3.100)}{=} \frac{1}{i\hbar}\langle\psi_H|[\hat{A}_H, \hat{H}_H]|\psi_H\rangle + \langle\psi_H|\partial_t\hat{A}_H|\psi_H\rangle \\ &= \frac{1}{i\hbar}\langle[\hat{A}_H, \hat{H}_H]\rangle + \langle\partial_t A_H\rangle \end{aligned}$$

Since this eq. holds also in Schrödinger picture we can write

$$\frac{d}{dt}\langle A\rangle = \frac{1}{i\hbar}\langle[\hat{A}, \hat{H}]\rangle + \langle\partial_t A\rangle \tag{3.103}$$

(same structure as eq. (3.100))

in particular we find

$$\frac{d}{dt}\langle x_i\rangle = \frac{1}{i\hbar}\langle[\hat{x}_i,\hat{H}]\rangle \overset{(3.79)}{=} \langle\frac{\partial\hat{H}}{\partial\hat{p}_i}\rangle \tag{3.104}$$

$$\frac{d}{dt}\langle p_i\rangle = \frac{1}{i\hbar}\langle[\hat{p}_i,\hat{H}]\rangle = -\langle\frac{\partial\hat{H}}{\partial\hat{x}_i}\rangle \tag{3.105}$$

$\longrightarrow$ Ehrenfest's Equations

Do they imply that the expectation values of position and momentum move classically? $\longrightarrow$ Not quite!

Examples:

(i) $\hat{H} = \frac{\hat{p}^2}{2m}$

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m}\ ; \quad \frac{d}{dt}\langle p\rangle = 0$$

$$\longrightarrow \langle x\rangle(t) = \frac{\langle p\rangle}{m}t + \langle x_0\rangle$$

classical motion!

(ii) $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m}{2}\omega^2\hat{x}^2$ (harmonic oscillator)

$$\frac{d}{dt}\langle x\rangle = \frac{\langle p\rangle}{m}\ ; \quad \frac{d}{dt}\langle p\rangle = -m\omega^2\langle x\rangle$$

$$\hookrightarrow \frac{d^2}{dt^2}\langle x\rangle + \omega^2\langle x\rangle = 0$$

(classical motion!)

(iii) but: $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$

in general $$\frac{d}{dt}\langle p\rangle = -\langle\frac{\partial V}{\partial x}\rangle = \langle F(x)\rangle \neq F(\langle x\rangle)$$

only if the latter inequality becomes an equality (free particle, harmonic oscillator) do $\langle x\rangle$, $\langle p\rangle$ obey classical equations of motion!

g) Energy-time uncertainty relation (cf. page 72)

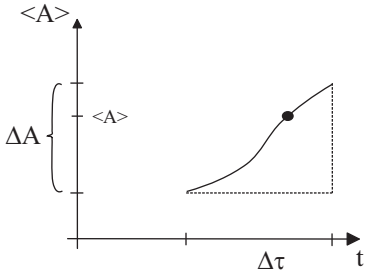
We have the general uncertainty relation eq. (3.83), and, in particular:

$$\Delta A\ \Delta E \geq \frac{1}{2}|\langle[\hat{A},\hat{H}]\rangle|$$

for any observable

If $\partial_t \hat{A} = 0$ we can use eq.(3.103) and obtain

$$\Delta A \; \Delta E \geq \frac{\hbar}{2} |d_t \langle \hat{A} \rangle|$$



Define time interval $\Delta\tau$ via

$$\frac{\Delta A}{\Delta \tau} \; = \; |\frac{d}{dt} \langle \hat{A} \rangle|$$

$$\boxed{\quad \Longrightarrow \quad \Delta E \; \Delta \tau \geq \frac{\hbar}{2} \qquad (3.106) \quad}$$

Interpretation: properties of a system change noticeably during $\Delta\tau$ only if $\Delta\tau \geq \frac{\hbar}{2\Delta E}$ (stationary states: $\Delta E = 0 \quad \hookrightarrow \quad \Delta\tau \; \rightarrow \; \infty$)
application: lifetimes (e.g. of excited states) + energy widths ('line widths')

3.4.3 Interaction picture

$\longrightarrow$ defined as lying 'in between' Schrödinger and Heisenberg pictures

S-picture		I-picture		H-picture
$\|\psi_S(t)\rangle$	$\overset{\hat{U}_0^\dagger(t,t_0),\ \hat{H}_0}{\longrightarrow}$	$\|\psi_I(t)\rangle$	$\overset{\hat{U}_I^\dagger(t,t_0),\ \hat{V}}{\longrightarrow}$	$\|\psi_H\rangle$
$\hat{A}_S$		$\hat{A}_I(t)$		$\hat{A}_H(t)$
$\searrow$				$\nearrow$
	$\longrightarrow\longrightarrow$	$\overset{\hat{U}^\dagger(t,t_0),\ \hat{H}}{\longrightarrow}$	$\longrightarrow\longrightarrow$	

we consider decomposition

$$\hat{H} \; = \; \hat{H}_0 + \hat{V} \qquad (3.107)$$

$$\hat{U}(t,t_0) \; = \; \hat{U}_0(t,t_0)\hat{U}_I(t,t_0) \qquad (3.108)$$

eqs. of motion :

$$\begin{aligned} i\hbar d_t \hat{U}_0(t,t_0) &= \hat{H}_0 \hat{U}_0(t,t_0) \\ \hat{U}_0(t_0,t_0) &= \hat{1} \\ i\hbar d_t \hat{U}(t,t_0) &= \hat{H}\hat{U}(t,t_0) \\ \hat{U}(t_0,t_0) &= \hat{1} \end{aligned}$$

Use them in eq. (3.108) (which defines $\hat{U}_I$):

$$\begin{aligned} i\hbar d_t\hat{U}(t,t_0) &= i\hbar(d_t\hat{U}_0)\hat{U}_I + \hat{U}_0 i\hbar d_t\hat{U}_I \\ &= \hat{H}_0\hat{U}_0\hat{U}_I + \hat{U}_0 i\hbar d_t\hat{U}_I \\ &= \hat{H}\hat{U}_0\hat{U}_I \end{aligned}$$

$$\iff \quad i\hbar d_t\hat{U}_I(t,t_0) = \hat{U}_0^\dagger(t,t_0)(\underbrace{\hat{H}-\hat{H}_0}_{=\hat{V}})\hat{U}_0(t,t_0)\hat{U}_I(t,t_0)$$

define, in general, transformed operators

$$\hat{A}_I(t) = \hat{U}_0^\dagger(t,t_0)\hat{A}_S(t)\hat{U}_0(t,t_0) \tag{3.109}$$

and states

$$|\psi_I(t)\rangle = \hat{U}_0^\dagger(t,t_0)|\psi_S(t)\rangle \tag{3.110}$$

$$\begin{aligned} \implies \quad i\hbar d_t\hat{U}_I(t,t_0) &= \hat{V}_I(t)\hat{U}_I(t,t_0) && (3.111)\\ \hat{U}_I(t_0,t_0) &= \hat{1} && (3.112) \end{aligned}$$

$\hat{U}_I$ can be interpreted as evolution operator in interaction picture

$$\begin{aligned} \text{moreover :} \qquad |\psi_I(t)\rangle &= \hat{U}_0^\dagger(t,t_0)|\psi_S(t)\rangle \\ &= \hat{U}_I(t,t_0)|\psi_H\rangle \\ &\overset{!}{=} \hat{U}_I(t,t_0)|\psi_I(t_0)\rangle && (3.113)\\ (\longrightarrow \quad |\psi_I(t_0)\rangle &\equiv |\psi_S(t_0)\rangle \equiv |\psi_H\rangle\ ) \end{aligned}$$

Differentiate eq. (3.113):

$$\begin{aligned} i\hbar d_t|\psi_I(t)\rangle &= \Big(i\hbar d_t\hat{U}_I(t,t_0)\Big)|\psi_I(t_0)\rangle \\ &= \hat{V}_I(t)\hat{U}_I(t,t_0)|\psi_I(t_0)\rangle \end{aligned}$$

$$\implies \quad i\hbar d_t|\psi_I(t)\rangle = \hat{V}_I(t)|\psi_I(t)\rangle \tag{3.114}$$

Schrödinger-type equation in interaction picture

Similarly, we obtain an equation of motion for operators (3.109)

$$i\hbar d_t\hat{A}_I(t) = [\hat{A}_I, \hat{H}_I^0] + i\hbar\partial_t\hat{A}_I \tag{3.115}$$

Characteristics of interaction picture:

- states and operators are time-dependent
- states are driven by $\hat{V}_I$ (eq. (3.114))
- operators are driven by $\hat{H}_I^0$ (eq. (3.115))

Literature: a thorough discussion of S-, I- and H-pictures can be found in: [Fic], chap. 3.5

3.5 Symmetries

"*Ein Ding ist symmetrisch, wenn es eine Möglichkeit gibt, es zu verändern, und es hinterher doch wieder so aussieht wie vorher.*"
H. Weyl nach R.P. Feynman, 'Vom Wesen physikalischer Gesetze', Kapitel 4

'translation':

$\hookrightarrow$ symmetry transformation: $\Longleftrightarrow$ operation which leaves some mathematical expressions or laws invariant

classical physics: symmetry transformation $\overset{\text{Noether theorem}}{\longleftrightarrow}$ conservation laws (i.e. constants of motion)

important examples: + special cases
invariance with respect to:

translations	$\longleftrightarrow$	momentum conservation
rotations	$\longleftrightarrow$	angular momentum conservation
translations in time	$\longleftrightarrow$	energy conservation

$\longrightarrow$ we will find analogous relations in QM!

3.5.1 Representation of symmetry transformations

We restrict the discussion to symmetry transformations which are mediated by linear operators (the other important case which we omit are transformations that are expressed by 'anti-linear' operators).

a) Transformation of states

$$|\tilde{\psi}\rangle = \hat{S}|\psi\rangle \tag{3.116}$$

require norm conservation:

$$\begin{aligned} \langle\tilde{\psi}|\tilde{\psi}\rangle &= \langle\psi|\hat{S}^\dagger\hat{S}|\psi\rangle = \langle\psi|\psi\rangle \\ \Longrightarrow \quad \hat{S}^\dagger &= \hat{S}^{-1} \end{aligned}$$

$\hookrightarrow$ linear symmetry transformations are represented by unitary operators (cf. page 47)

b) Transformation of operators

$$\hat{\tilde{A}} = \hat{S}\hat{A}\hat{S}^\dagger \tag{3.117}$$

such that $\langle\tilde{\psi}|\hat{\tilde{A}}|\tilde{\psi}\rangle = \langle\psi|\hat{A}|\psi\rangle$

Consequences:

1. $\hat{A}|a_n\rangle = a_n|a_n\rangle$

$$\hookrightarrow \quad \hat{\tilde{A}}|\tilde{a}_n\rangle = \hat{S}\hat{A}\hat{S}^\dagger\hat{S}|a_n\rangle = a_n\hat{S}|a_n\rangle = a_n|\tilde{a}_n\rangle$$

(same eigenvalues)

2. $\omega_n = |\langle a_n|\psi\rangle|^2 = |\langle\tilde{a}_n|\tilde{\psi}\rangle|^2$
(same 'transition' probabilities)

i.e. if 'everything' is transformed simultaneously, physics remains unchanged!

c) Some properties of symmetry operators $\hat{S}$

1. they can be written as

$$\hat{S} = e^{i\hat{O}} \tag{3.118}$$

$$\hat{S}^{-1} = \hat{S}^\dagger \quad \Longleftrightarrow \quad \hat{O} = \hat{O}^\dagger$$

(proof: [Blöc], chap. 9)

$$\Longrightarrow \quad [\hat{S}, \hat{O}] = 0$$

2. $\hat{S}|\sigma_n\rangle = e^{i\hat{O}}|\sigma_n\rangle = e^{i\sigma_n}|\sigma_n\rangle$, $(\sigma_n \in \mathbb{R})$
$\hookrightarrow$ i.e. common eigenvectors, and eigenvalues of $\hat{S}$ are of modulus 1

3. Symmetry transformations (and - apart from exceptions - operators $\hat{S}$) form (not necessarily abelian) groups
$\longrightarrow$ group theory is a powerful approach to the investigation of symmetries (see, e.g., [Mes] QM II, App. D and chap. 15)

3.5.2 Symmetries and constants of motion

a) Definition: operator $\hat{A}$ is called symmetrical (invariant) with respect to $\hat{S}$

$$\begin{aligned} :\Longleftrightarrow \quad & \hat{\tilde{A}} = \hat{S}\hat{A}\hat{S}^\dagger = \hat{A} \\ \Longleftrightarrow \quad & [\hat{A}, \hat{S}] = 0 \end{aligned} \tag{3.119}$$

$$\begin{aligned} \hookrightarrow \quad \langle\psi|\hat{A}|\psi\rangle &= \langle\psi|\hat{\tilde{A}}|\psi\rangle \\ &= \langle\psi|\hat{S}\hat{A}\hat{S}^\dagger|\psi\rangle \\ &= \langle\tilde{\tilde{\psi}}|\hat{A}|\tilde{\tilde{\psi}}\rangle \\ &\qquad (\text{ with } |\tilde{\tilde{\psi}}\rangle = \hat{S}^\dagger|\psi\rangle \text{ }) \end{aligned}$$

i.e. transformation of $\hat{A}$ yields same expectation value as inverse transformation of state

b) Invariance of the TDSE (3.87)

$$\begin{aligned} \text{transformation} \qquad |\tilde{\psi}\rangle &= \hat{S}|\psi\rangle \\ \text{consider} \qquad i\hbar d_t|\tilde{\psi}\rangle &= i\hbar d_t(\hat{S}|\psi\rangle) \\ &= i\hbar(\partial_t\hat{S})|\psi\rangle + \hat{S}i\hbar\partial_t|\psi\rangle \\ &= (i\hbar\partial_t\hat{S} + \hat{S}\hat{H})|\psi\rangle \\ \text{invariance means that :} \qquad &\stackrel{!}{=} \hat{H}|\tilde{\psi}\rangle = \hat{H}\hat{S}|\psi\rangle \end{aligned}$$

(i.e. transformed state fulfills TDSE with the same Hamiltonian!)

$$\Longleftrightarrow \quad i\hbar\partial_t\hat{S} + [\hat{S}, \hat{H}] = 0 \tag{3.120}$$

Note that this equation holds also in the Heisenberg picture (although we have derived it in the Schrödinger picture). In fact, one can extract it also from the requirement that the Heisenberg equation (3.100) be invariant with respect to $\hat{S}$.

Now, let's compare eq. (3.120) with 'standard Heisenberg equation' (3.100) for $\hat{S}$.

$$\Longrightarrow \quad \text{invariance of equation of motion} \quad \Longleftrightarrow \quad d_t\hat{S}_H = 0 \tag{3.121}$$

Note that $\hat{S}$ is no observable; but $\hat{O}$ (eq. (3.118)) is, and it is straightforward to show that $d_t\hat{S}_H = 0$ implies $d_t\hat{O}_H = 0$

> $\hookrightarrow$ If TDSE is invariant with respect to transformation $\hat{S}$
> $\longrightarrow$ hermitian operators $\hat{O}$ which are defined via $\hat{S}$ are constants of motion[5]

in closed systems, we have $\partial_t\hat{O} = \partial_t\hat{S} = 0$

$$\hookrightarrow \quad \hat{O} \text{ is constant of motion} \quad \Longleftrightarrow \quad [\hat{O},\hat{H}] = 0 = [\hat{S},\hat{H}] \quad \Longleftrightarrow \quad [\hat{O},\hat{U}(t,t_0)] = 0 \tag{3.122}$$

(cf. eq. (3.102))

c) Recipe for discussion of stationary problems

(a) Write down $\hat{H}$
(b) Find symmetry transformations via $[\hat{S},\hat{H}] = 0$
(c) Find generators $\hat{O}$ (which are constants of motion)
(d) Find simultaneous eigenstates of $\hat{S},\hat{O},\hat{H}$

3.5.3 Translations (1-d)

Let's consider translations in real space as an example of a continuous symmetry transformation.
Obviously we have:
translation ξ_1 + translation ξ_2 = translation $\xi_1+\xi_2$ = translation ξ_2 + translation ξ_1
$\longrightarrow$ translations form a continuous abelian group!

$\hookrightarrow$ translation operator

$$\hat{T}(\xi_1)\hat{T}(\xi_2) = \hat{T}(\xi_2)\hat{T}(\xi_1) = \hat{T}(\xi_1+\xi_2) \tag{3.123}$$

$\longrightarrow$ eq. (3.123) is solved by

$$\hat{T}(\xi) = e^{i\xi\hat{G}}, \quad (\hat{G} = \hat{G}^\dagger) \tag{3.124}$$

- Infinitesimal translation

$$\hat{T}(\delta\xi) = \hat{1} + i\delta\xi\hat{G}$$
$$\Longleftrightarrow \quad \hat{G} = -i\,\frac{\hat{T}(\delta\xi)-\hat{T}(0)}{\delta\xi} = -i\,\frac{d\hat{T}}{d\xi}\bigg|_{\xi=0} \tag{3.125}$$

[5] $\hat{O}$ is called 'generator' of symmetry transformation

- Action on states (this is an obvious postulate)

$$\hat{T}(\xi)|x\rangle = |x+\xi\rangle = |\tilde{x}\rangle \tag{3.126}$$
$$\hat{T}^\dagger(\xi)|x\rangle = |x-\xi\rangle \tag{3.127}$$

$$\begin{aligned} \hookrightarrow \quad \tilde{\psi}(x) &= \langle x|\tilde{\psi}\rangle = \langle x|\hat{T}(\xi)|\psi\rangle = \langle \hat{T}^\dagger(\xi)x|\psi\rangle \\ &= \langle x-\xi|\psi\rangle = \psi(x-\xi) \end{aligned} \tag{3.128}$$

Transformed wave function at x = original wave function at inversely transformed position $x-\xi$

- Action on $\hat{x}$

$$\begin{aligned} \lhd \qquad \langle\tilde{\psi}|\hat{x}|\tilde{\psi}\rangle &= \langle\hat{T}\psi|\hat{x}|\hat{T}\psi\rangle = \langle\psi|\hat{T}^\dagger\hat{x}\hat{T}|\psi\rangle \\ &= \int \langle\tilde{\psi}|x\rangle\langle x|\hat{x}|x'\rangle\langle x'|\tilde{\psi}\rangle \, dxdx' \\ &= \int \tilde{\psi}^*(x)x\tilde{\psi}(x) \, dx \\ &\overset{(3.128)}{=} \int \psi^*(x-\xi)x\psi(x-\xi) \, dx \\ &\overset{x-\xi\to x}{=} \int \psi^*(x)(x+\xi)\psi(x) \, dx \\ &= \langle\psi|\hat{x}+\xi\hat{1}|\psi\rangle \end{aligned}$$

compare:

$$\hat{T}^\dagger(\xi)\hat{x}\hat{T}(\xi) = \hat{x}+\xi\hat{1} \tag{3.129}$$
$$\hat{T}(\xi)\hat{x}\hat{T}^\dagger(\xi) = \hat{x}-\xi\hat{1} \tag{3.130}$$

- Consider infinitesimal transformation

$$\begin{aligned} \hat{T}(\delta\xi)\hat{x}\hat{T}^\dagger(\delta\xi) &= (\hat{1}+i\delta\xi\hat{G})\hat{x}(\hat{1}-i\delta\xi\hat{G}) \\ &= \hat{x}+i\delta\xi[\hat{G},\hat{x}]+O(\delta\xi^2) \\ &\overset{(3.130)}{=} \hat{x}-\delta\xi\hat{1} \\ \implies \quad [\hat{G},\hat{x}] &= i \end{aligned} \tag{3.131}$$

Define:

$$\hat{p} = -\hbar\hat{G} \,, \qquad (\hat{p} \text{ has dimension of momentum})$$

$$\begin{aligned} \implies \quad \hat{T}(\xi) &= e^{-\frac{i}{\hbar}\xi\hat{p}} \\ [\hat{x},\hat{p}] &= i\hbar \end{aligned} \tag{3.132}$$

i.e. one can derive the basic commutator $[\hat{x}, \hat{p}]$, which was postulated in chapter 3.3.5 from consideration of symmetry transformation

- $\lhd$
$$\begin{aligned}
\hat{p}_{(x)}\psi(x) &= \langle x|\hat{p}|\psi\rangle = \int \langle x|\hat{p}|x'\rangle\psi(x')\,dx \\
&\overset{(3.125)}{=} i\hbar \int \langle x| \left.\frac{d\hat{T}}{d\xi}\right|_{\xi=0} |x'\rangle\psi(x')\,dx' \\
&= i\hbar \lim_{\xi\to 0} \int \langle x| \frac{\hat{T}(\xi) - \hat{T}(0)}{\xi} |x'\rangle\psi(x')\,dx' \\
&= i\hbar \lim_{\xi\to 0} \int \frac{\langle x|x'+\xi\rangle - \langle x|x'\rangle}{\xi}\psi(x')\,dx' \\
&= i\hbar \int d_{x'}\delta(x-x')\psi(x')\,dx' \\
&= -i\hbar d_x \psi(x)
\end{aligned}$$

$\longrightarrow$ standard form of $\hat{p}_{(x)}$ is recovered from definition and properties of translations.

Some comments:

1. Structure of theory

   1st step: consider symmetry transformations; i.e. define and investigate translations
   $\hookrightarrow$ derive $[\hat{x}, \hat{p}] = i\hbar$
   $\hookrightarrow$ further consequences (see chapter 3.2.3)

2. if $[\hat{H}, \hat{T}(\xi)] = 0$ (translational invariance)
   $\Longrightarrow$ momentum conservation (cf. eq. (3.122))

   e.g. $\quad \hat{H} = \dfrac{\hat{p}^2}{2m} \quad \longrightarrow \quad [\hat{H}, \hat{T}] = [\hat{H}, \hat{p}] = 0$

   $\hat{H} = \dfrac{\hat{p}^2}{2m} + \hat{V}(x) \quad \longrightarrow \quad [\hat{H}, \hat{T}] = [\hat{V}, \hat{T}] \neq 0$

3.5.4 Other continuous symmetry transformations

a) Rotations

- about a fixed axis $\longrightarrow$ abelian group

  e.g. $\quad \hookrightarrow \quad \hat{R}_z(\alpha) = e^{-\frac{i}{\hbar}\alpha\hat{l}_z}$ (3.133)

one finds that generator can be identified with corresponding component of angular momentum operator

if	$[\hat{H}, \hat{R}_z(\alpha)] = 0$	$\longrightarrow$	$\hat{l}_z$ is conserved!
i.e. rotational invariance		$\longrightarrow$	angular momentum conservation

- general rotations:
  more difficult!
  But: each rotation can be composed from three (non-commuting) rotations about 'Euler angles' (cf. Classical Mechanics)
  One finds correspondingly:

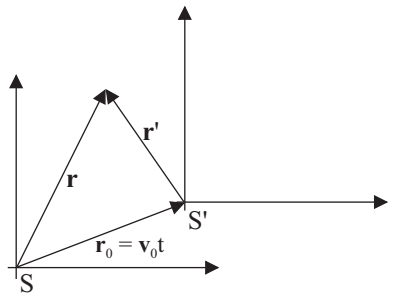
$$\hookrightarrow \quad \hat{R}(\alpha\beta\gamma) = e^{-\frac{i}{\hbar}\alpha\hat{l}_z} e^{-\frac{i}{\hbar}\beta\hat{l}_y} e^{-\frac{i}{\hbar}\gamma\hat{l}_z} \tag{3.134}$$

and

$$[\hat{l}_i, \hat{l}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{l}_k \ , \qquad \text{(cf. eq. (3.82))}$$

as rotations about different axes do not commute.

b) Galilei transformations



consider translation of coordinate system

$$\begin{aligned} \hookrightarrow \quad \mathbf{r}' &= \mathbf{r} - \mathbf{v}t \\ \mathbf{p}' &= \mathbf{p} - m\mathbf{v} \end{aligned}$$

$\longrightarrow$ corresponding operators (requires some calculation)

$$\hat{\mathbf{r}}' = \hat{\Gamma}(\mathbf{v})\hat{\mathbf{r}}\hat{\Gamma}^\dagger(\mathbf{v}) = \hat{\mathbf{r}} - \mathbf{v}t\hat{1} \tag{3.135}$$

$$\hat{\mathbf{p}}' = \hat{\Gamma}(\mathbf{v})\hat{\mathbf{p}}\hat{\Gamma}^\dagger(\mathbf{p}) = \hat{\mathbf{p}} - \mathbf{v}m\hat{1} \tag{3.136}$$

with

$$\hat{\Gamma}(\mathbf{v}) = \exp\left[\frac{i}{\hbar}\mathbf{v}(m\hat{\mathbf{r}} - t\hat{\mathbf{p}})\right] \tag{3.137}$$

'Galilei operator' depends on time explicitly!

$\longrightarrow$ invariance of TDSE if (cf. eq. (3.120))

$$i\hbar\partial_t\hat{\Gamma}(\mathbf{v}) + [\hat{\Gamma}(\mathbf{v}), \hat{H}] = 0$$

3.5.5 Discrete symmetry transformations

a) Reflections $\longrightarrow$ parity

the simplest symmetry group (only two elements) is obtained from definition

$$\begin{aligned} \hat{S}_0|\mathbf{r}\rangle &= |-\mathbf{r}\rangle \qquad (3.138)\\ \hookrightarrow \quad \hat{S}_0^2|\mathbf{r}\rangle &= |\mathbf{r}\rangle \\ \hookrightarrow \quad \hat{S}_0 &= \hat{S}_0^{-1} = \hat{S}_0^\dagger \qquad (3.139) \end{aligned}$$

symmetry operator is unitary and hermitian
$\hookrightarrow$ apply it to wave function

$$\hat{S}_0\psi(\mathbf{r}) = \langle\mathbf{r}|\hat{S}_0|\psi\rangle = \langle\hat{S}_0\mathbf{r}|\psi\rangle = \psi(-\mathbf{r})$$

- eigenvalue equations:
  $\longrightarrow$ $\hat{S}_0$ is unitary: modulus of eigenvalues $= \hat{1}$ (page 83)
  $\longrightarrow$ $\hat{S}_0$ is hermitian: eigenvalues real
  $\hookrightarrow$ eigenvalues ± 1

$$\begin{aligned} \hat{S}_0|\psi_\pm\rangle &= \pm|\psi_\pm\rangle \qquad (3.140)\\ + &: \text{positive (even) 'parity'} \\ - &: \text{negative (odd) 'parity'} \end{aligned}$$

if $[\hat{S}_0, \hat{H}] = 0 \quad \longrightarrow \quad$ parity conservation

(not fulfilled in case of weak interactions $\longrightarrow$ parity violation in β-decay)

b) Discrete translations $\longrightarrow$ Bloch-theorem

Simple model of a crystal: atomic sites are fixed and form a periodic lattice; electrons move independently in a model potential which is also periodic

task: solve (stationary) Schrödinger eq. for an electron in periodic potential

$$V(\mathbf{r}+\mathbf{t}) = V(\mathbf{r}) \qquad (3.141)$$

$\mathbf{t}$ is an arbitrary lattice-translation vector (see [Blöc], chap. 10.5)

$\hookrightarrow$ discrete translation (cf. eq. (3.126), (3.127))

$$\begin{aligned} \hat{T}|\mathbf{r}\rangle &= |\mathbf{r}+\mathbf{t}\rangle \qquad (3.142)\\ \longrightarrow \quad \hat{T}_{(\mathbf{r})}\psi(\mathbf{r}) &= \langle\mathbf{r}|\hat{T}|\psi\rangle = \psi(\mathbf{r}-\mathbf{t}) \end{aligned}$$

if $\qquad V(\mathbf{r}) = V(\mathbf{r}+\mathbf{t}) \quad \hookrightarrow \quad [\hat{H}, \hat{T}] = 0$

search for common eigenstates $\psi(\mathbf{r})$:

$\lhd$ eigenvalue eq. of $\hat{T}$ (in coordinate space)

$$\hat{T}_{(\mathbf{r})}\psi(\mathbf{r}) = e^{-i\mathbf{kt}}\psi(\mathbf{r}) \tag{3.143}$$

(defines $\mathbf{k}$ implicitly)

together with eq. (3.142):

$$\begin{aligned} \psi(\mathbf{r}-\mathbf{t}) &= e^{-i\mathbf{kt}}\psi(\mathbf{r}) \\ \Longleftrightarrow \quad \psi(\mathbf{r}) &= e^{i\mathbf{kt}}\psi(\mathbf{r}-\mathbf{t}) \\ \text{ansatz}: \quad \psi(\mathbf{r}) &= e^{i\mathbf{kr}}u_{\mathbf{k}}(\mathbf{r}) \\ \hookrightarrow \quad \psi(\mathbf{r}) &= e^{i\mathbf{kt}}e^{i\mathbf{k}(\mathbf{r}-\mathbf{t})}u_{\mathbf{k}}(\mathbf{r}-\mathbf{t}) \end{aligned} \tag{3.144}$$

$$\boxed{u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}-\mathbf{t})} \tag{3.145}$$

Bloch theorem: Eigenfunctions of periodic systems are of the form $\psi(\mathbf{r}) = e^{i\mathbf{kr}}u_{\mathbf{k}}(\mathbf{r})$ with $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}-\mathbf{t})$ (i.e. periodic functions)

Use it in Schrödinger eq.

$$\Big(-\frac{\hbar^2}{2m}\Delta + V(\mathbf{r})\Big)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$$\hookrightarrow \quad \Big(\underbrace{-\frac{\hbar^2}{2m}(\boldsymbol{\nabla}+i\mathbf{k})^2 + V(\mathbf{r})}_{\hat{H}'(\mathbf{k})}\Big)u^n_{\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})u^n_{\mathbf{k}}(\mathbf{r}) \tag{3.146}$$

the new Hamiltonian $\hat{H}'$ depends continuously on $\mathbf{k}$

$\longrightarrow$ $E_n(\mathbf{k})$: dispersion relations of electrons in periodic potential (cf. dispersion relation of free particles (eq. (2.24)))
$\longrightarrow$ band structure

c) Permutations of identical particles

identical particles share all physical properties, e.g. mass, charge; their permutations are connected with a symmetry property

Consider two identical particles ($N = 2$)

Preparation:

- Some remarks on direct product states and spaces

  consider states $|\varphi^{(1)}\rangle \in \mathcal{H}^{(1)}$, $|\varphi^{(2)}\rangle \in \mathcal{H}^{(2)}$

  define direct product:

$$\begin{aligned} & |\varphi^{(1)}\varphi^{(2)}\rangle = |\varphi^{(1)}\rangle|\varphi^{(2)}\rangle = |\varphi^{(2)}\rangle|\varphi^{(1)}\rangle \\ \hookrightarrow \quad & |\varphi^{(1)}\varphi^{(2)}\rangle \in \mathcal{H} = \mathcal{H}^{(1)} \times \mathcal{H}^{(2)} \end{aligned}$$

  scalar product in $\mathcal{H}$:

  $\langle\varphi^{(1)}\varphi^{(2)}|\psi^{(1)}\psi^{(2)}\rangle = \langle\varphi^{(1)}|\psi^{(1)}\rangle\langle\varphi^{(2)}|\psi^{(2)}\rangle$ (satisfies axioms, chapter 3.1.1)

  if $\{|\varphi_k^{(1)}\rangle\}$ ONB (orthonormal basis) in $\mathcal{H}_1$ and $\{|\varphi_l^{(2)}\rangle\}$ ONB in $\mathcal{H}_2$

$$\Longrightarrow \quad \{|\varphi_k^{(1)}\varphi_l^{(2)}\rangle\} \quad \text{ONB in } \mathcal{H}$$

$$\text{i.e.} \quad |\Psi\rangle = \sum_{kl} c_{kl}|\varphi_k^{(1)}\varphi_l^{(2)}\rangle \quad \text{for all} \quad |\Psi\rangle \in \mathcal{H}$$

  if dimensions of spaces are finite

$$\hookrightarrow \quad \dim\ \mathcal{H} = (\dim\ \mathcal{H}_1)(\dim\ \mathcal{H}_2)$$

  Operators:

$$\begin{aligned} \text{if} \quad & \hat{A}^{(1)}|\varphi^{(1)}\rangle = |\chi^{(1)}\rangle \\ \text{then} \quad & \hat{A}^{(1)}|\varphi^{(1)}\varphi^{(2)}\rangle = |\chi^{(1)}\varphi^{(2)}\rangle \end{aligned}$$

  (i.e. $\hat{A}^{(1)}$ does not act on $|\varphi^{(2)}\rangle$)

$$\Longrightarrow \quad [\hat{A}^{(1)}, \hat{B}^{(2)}] = 0$$

  but: there are operators that act on both $|\varphi^{(1)}\rangle$ and $|\varphi^{(2)}\rangle$
  Define permutation operator $\hat{P}_{12}$

$$\hat{P}_{12}|\Psi(1,2)\rangle = |\Psi(2,1)\rangle \tag{3.147}$$

  (coordinate representation $\langle\mathbf{r}_1\mathbf{r}_2|\Psi\rangle = \Psi(\mathbf{r}_1\mathbf{r}_2)$)

$$\text{obviously} \quad \hat{P}_{12}^2 = \hat{1} \quad \hookrightarrow \quad \hat{P}_{12} = \hat{P}_{12}^{-1} = \hat{P}_{12}^{\dagger} \tag{3.148}$$

(cf. parity operator eq. (3.139))

$\hookrightarrow$ eigenvalue problem (similar to the one of $\hat{S}_0$)

$$\hat{P}_{12}|\Psi^+(1,2)\rangle = |\Psi^+(1,2)\rangle \ , \qquad (\text{'symmetrical'}) \tag{3.149}$$
$$\hat{P}_{12}|\Psi^-(1,2)\rangle = -|\Psi^-(1,2)\rangle \ , \qquad (\text{'antisymmetrical'}) \tag{3.150}$$

states

All known Hamiltonians commute with $\hat{P}_{12}$: $[\hat{H}, \hat{P}_{12}] = 0$
Moreover, we postulate that all observables commute with all permutation operators $\hat{P}_\sigma$ of a many-particle system (if particles are identical)

symmetrization postulate

$$[\hat{P}_\sigma, \hat{O}] = 0 \ , \quad \forall \ \hat{O}, \hat{P}_\sigma \tag{3.151}$$

Implication: there is no way to distinguish identical particles in QM (no observable is sensitive to permutations)

$\Longrightarrow$ QM states are either (totally) symmetric or (totally) antisymmetric with respect to particle exchange, i.e.

$$\text{either} \quad \hat{P}_\sigma|\Psi^+\rangle = |\Psi^+\rangle \qquad \text{for all permutations}$$
$$\text{or} \quad \hat{P}_{ij}|\Psi^-\rangle = -|\Psi^-\rangle \qquad \text{for all transpositions}$$

This statement is very important and has no classical analogy. It must be fulfilled since otherwise the projector $|\Phi\rangle\langle\Phi|$ on a non-(anti-)symmetric state $|\Phi\rangle$ would not commute with all permutation operators (i.e. would violate eq. (3.151))!
A simple example: two non-interacting particles in common potential

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} = \frac{\hat{\mathbf{p}}_1^2}{2m} + V(\mathbf{r}_1) + \frac{\hat{\mathbf{p}}_2^2}{2m} + V(\mathbf{r}_2) \tag{3.152}$$

We assume that we know the single-particle solutions:

$$\hat{H}^{(1)}|\varphi_k^{(1)}\rangle = \epsilon_k^{(1)}|\varphi_k^{(1)}\rangle$$
$$\hat{H}^{(2)}|\varphi_l^{(2)}\rangle = \epsilon_l^{(2)}|\varphi_l^{(2)}\rangle$$

it follows that $|\Psi\rangle = |\varphi_k^{(1)}\varphi_l^{(2)}\rangle$ solves

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad \text{with} \quad E = \epsilon_k^{(1)} + \epsilon_l^{(2)}$$

proof:

$$\begin{aligned}\hat{H}|\varphi_k^{(1)}\varphi_l^{(2)}\rangle &= \Big(\hat{H}^{(1)}|\varphi_k^{(1)}\rangle\Big)|\varphi_l^{(2)}\rangle + |\varphi_k^{(1)}\rangle\hat{H}^{(2)}|\varphi_l^{(2)}\rangle \\ &= \Big(\epsilon_k^{(1)} + \epsilon_l^{(2)}\Big)|\varphi_k^{(1)}\varphi_l^{(2)}\rangle\end{aligned}$$

There is a second eigenstate with the same eigenenergy:

$$\begin{aligned}|\tilde{\Psi}\rangle = \hat{P}_{12}|\Psi\rangle = |\varphi_l^{(1)}\varphi_k^{(2)}\rangle \\ \longrightarrow \quad \text{exchange degeneracy}\end{aligned}$$

$|\Psi\rangle$, $|\tilde{\Psi}\rangle$ are not symmetric or antisymmetric (i.e. they don't fulfill eq. (3.149), (3.150))

$\hookrightarrow$ (Anti-) symmetric solutions (for $l \neq k$):

$$\begin{aligned}|\Psi^+\rangle &= \frac{1}{\sqrt{2}}\Big\{|\Psi\rangle + |\tilde{\Psi}\rangle\Big\} = \frac{1}{\sqrt{2}}\Big\{|\varphi_k^{(1)}\varphi_l^{(2)}\rangle + |\varphi_l^{(1)}\varphi_k^{(2)}\rangle\Big\} \\ |\Psi^-\rangle &= \frac{1}{\sqrt{2}}\Big\{|\Psi\rangle - |\tilde{\Psi}\rangle\Big\} = \frac{1}{\sqrt{2}}\Big\{|\varphi_k^{(1)}\varphi_l^{(2)}\rangle - |\varphi_l^{(1)}\varphi_k^{(2)}\rangle\Big\}\end{aligned} \qquad (3.153)$$

- properly normalized for $l \neq k$, ($\langle\Psi^+|\Psi^+\rangle = \langle\Psi^-|\Psi^-\rangle = 1$)
- for $l = k$ we have

$$\begin{aligned}|\Psi^+\rangle &= |\varphi_k^{(1)}\varphi_k^{(2)}\rangle\ , \quad (\langle\Psi^+|\Psi^+\rangle = 1) \\ |\Psi^-\rangle &= 0 \qquad \longrightarrow \quad \text{Pauli principle!}\end{aligned}$$

- Antisymmetric product states
  We can rewrite $|\Psi^-\rangle$ of eq. (3.153) in the form of a determinant:

$$|\Psi^-\rangle = \frac{1}{\sqrt{2}}\begin{vmatrix} |\varphi_k^{(1)}\rangle & |\varphi_k^{(2)}\rangle \\ |\varphi_l^{(1)}\rangle & |\varphi_l^{(2)}\rangle \end{vmatrix}$$

This can be generalized ($N \geq 2$):

$$|\Psi^-\rangle = \frac{1}{\sqrt{N!}}\begin{vmatrix} |\varphi_{k_1}^{(1)}\rangle & \dots & |\varphi_{k_1}^{(N)}\rangle \\ \vdots & & \\ |\varphi_{k_N}^{(1)}\rangle & \dots & |\varphi_{k_N}^{(N)}\rangle \end{vmatrix} \qquad (3.154)$$

"Slater determinant" ($\langle\Psi^-|\Psi^-\rangle = 1$, if $\langle\varphi_{k_i}|\varphi_{k_j}\rangle = \delta_{ij}$)

determinant is zero if two lines or two columns are identical

$\hookrightarrow$	Pauli principle: (for antisymmetric states)	two particles of a system of N identical particles cannot occupy the same single-particle state $\|\varphi_{k_i}\rangle$!

Even though we have only considered non-interacting systems so far, we can formulate the Pauli principle for the case of interacting particles in a similar way:

Let's consider:

- Interacting two-particle systems

$$\hat{H} = \hat{H}^{(1)} + \hat{H}^{(2)} + \hat{W}(1,2) \tag{3.155}$$

$\hookrightarrow$ Schrödinger eq. $\hat{H}|\Psi\rangle = E|\Psi\rangle$ cannot be separated, but symmetrization postulate (3.151) is still valid.

$$\hookrightarrow \quad |\Psi^{\pm}\rangle = \sum_{kl} c_{kl}^{(\pm)} |\varphi_k^{(1)} \varphi_l^{(2)}\rangle \tag{3.156}$$

i.e. the physical solutions are either symmetric or antisymmetric and can be expanded in the basis $\left\{|\varphi_k^{(1)}\varphi_l^{(2)}\rangle\right\}$
(note that $|\Psi^-\rangle$ is no longer a single Slater determinant)

E.g. in coordinate representation we can write:

$$\begin{aligned} \langle \mathbf{r}_1 ... \mathbf{r}_N | \Psi^{(\pm)} \rangle &= \\ \Psi^{(\pm)}(\mathbf{r}_1 ... \mathbf{r}_i ... \mathbf{r}_j ... \mathbf{r}_N) &= \pm \Psi^{(\pm)}(\mathbf{r}_1 ... \mathbf{r}_j ... \mathbf{r}_i ... \mathbf{r}_N) \\ \hookrightarrow \quad \Psi^{-}(\mathbf{r}_1 ... \mathbf{r}_i ... \mathbf{r}_i ... \mathbf{r}_N) &= -\Psi^{-}(\mathbf{r}_1 ... \mathbf{r}_i ... \mathbf{r}_i ... \mathbf{r}_N) = 0 \end{aligned}$$

$\longrightarrow$ Pauli principle!

- Symmetry considerations show that only (anti-) symmetric many particle states exist in QM. Do they both exist in nature?

Yes, they do. Moreover, both 'kinds' of states are related to the spin (see chapter 3) of the particles:

Spin-statistics theorem (Pauli, 1940)

Symmetrical states "bosons"	$\longrightarrow$	Spin $= 0, 1, 2, ...$ (photons, mesons)
Antisymmetrical states "fermions"	$\longrightarrow$	Spin $= \frac{1}{2}, \frac{3}{2}, ...$ (e^-, p, n, quarks)

Shell structure of atoms follows from antisymmetric nature of electrons, which cannot occupy the same state.
Bosons do not avoid each other, they can occupy the same state, e.g. the ground state.
Such states have been realized recently for bosonic atoms (and, even more recently, molecules)

$\longrightarrow$ Bose-Einstein condensation

Chapter 4

Applications of the Theory

4.1 The harmonic oscillator

Important model system, because

- describes systems in the neighborhood of a stable equilibrium (see [Kira], chap. 3.2)
- mathematically exactly solvable in classical and quantum mechanics

4.1.1 Algebraic solution of the one-dimensional harmonic oscillator

Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{c}{2}\hat{x}^2 = \frac{1}{2m}(\hat{p}^2 + m^2\omega_0^2\hat{x}^2) \tag{4.1}$$

aim: solve $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

Rewrite $\hat{H}$:

$$\begin{aligned} \hat{H} &= \frac{1}{2m}\Big[(\hat{p} + im\omega_0\hat{x})(\hat{p} - im\omega_0\hat{x}) + im\omega_0(\underbrace{\hat{p}\hat{x} - \hat{x}\hat{p}}_{=\frac{\hbar}{i}})\Big] \\ &= \hbar\omega_0\left[\frac{(\hat{p} + im\omega_0\hat{x})(\hat{p} - im\omega_0\hat{x})}{2m\hbar\omega_0} + \frac{1}{2}\right] \end{aligned} \tag{4.2}$$

To proceed we need

a) Creation and annihilation operators
Definition:

$$\hat{a}^\dagger := \frac{1}{\sqrt{2m\hbar\omega_0}}(\hat{p} + im\omega_0\hat{x}) \tag{4.3}$$

"creation operator"

$$\hat{a} := \frac{1}{\sqrt{2m\hbar\omega_0}}(\hat{p} - im\omega_0\hat{x}) \tag{4.4}$$

"annihilation operator"

$$\hookrightarrow \quad (\hat{a}^\dagger)^\dagger = \hat{a}$$

$$\overset{(4.2)}{\hookrightarrow} \quad \boxed{\hat{H} = \hbar\omega_0(\hat{a}^\dagger\hat{a} + \frac{1}{2})} \tag{4.5}$$

alternative decomposition of $\hat{H}$:

$$\begin{aligned}\hat{H} &= \frac{1}{2m}\Big[(\hat{p} - im\omega_0\hat{x})(\hat{p} + im\omega_0\hat{x}) + im\omega_0[\hat{x}, \hat{p}]\Big] \\ &= \hbar\omega_0\left\{\frac{(\hat{p} - im\omega_0\hat{x})(\hat{p} + im\omega_0\hat{x})}{2m\hbar\omega_0} - \frac{1}{2}\right\} \\ &= \hbar\omega_0\Big(\hat{a}\hat{a}^\dagger - \frac{1}{2}\Big)\end{aligned} \tag{4.6}$$

Combine eqs. (4.5) and (4.6)

$$\begin{aligned}\hookrightarrow \quad \frac{\hat{H}}{\hbar\omega_0} &= \hat{a}\hat{a}^\dagger - \frac{1}{2} \\ \frac{\hat{H}}{\hbar\omega_0} &= \hat{a}^\dagger\hat{a} + \frac{1}{2}\end{aligned}$$

$$\overset{\text{subtract}}{\Longrightarrow} \quad \boxed{[\hat{a}, \hat{a}^\dagger] = \hat{1}} \tag{4.7}$$

$$\overset{\text{add}}{\Longrightarrow} \quad \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} = \frac{2}{\hbar\omega_0}\hat{H}$$

Definition: Anti-commutator

$$[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A}$$

$$\hookrightarrow \quad \boxed{[\hat{a}, \hat{a}^\dagger]_+ = \frac{2\hat{H}}{\hbar\omega_0}} \tag{4.8}$$

Some useful relations:

$$\begin{aligned}[\hat{a}, \hat{H}] &= \hbar\omega_0[\hat{a}, \hat{a}^\dagger\hat{a}] \\ &= \hbar\omega_0\Big\{[\hat{a}, \hat{a}^\dagger]\hat{a} + \hat{a}^\dagger[\hat{a}, \hat{a}]\Big\} \\ &= \hbar\omega_0\hat{a} \end{aligned} \tag{4.9}$$

$$\begin{aligned}[\hat{a}^\dagger, \hat{H}] &= \hbar\omega_0[\hat{a}^\dagger, \hat{a}\hat{a}^\dagger] \\ &= \hbar\omega_0\Big\{[\hat{a}^\dagger, \hat{a}]\hat{a}^\dagger + \hat{a}[\hat{a}^\dagger, \hat{a}^\dagger]\Big\} \\ &= -\hbar\omega_0\hat{a}^\dagger \end{aligned} \tag{4.10}$$

b) Energy spectra

$$\begin{aligned}\lhd \qquad \hat{H}\hat{a}|\psi_n\rangle &= \Big(\hat{a}\hat{H} - [\hat{a}, \hat{H}]\Big)|\psi_n\rangle \\ &= \hat{a}(\hat{H} - \hbar\omega_0)|\psi_n\rangle \\ &= (E_n - \hbar\omega_0)\hat{a}|\psi_n\rangle \end{aligned} \tag{4.11}$$

$$\begin{aligned}\lhd \qquad \hat{H}\hat{a}^\dagger|\psi_n\rangle &= \Big(\hat{a}^\dagger\hat{H} - [\hat{a}^\dagger, \hat{H}]\Big)|\psi_n\rangle \\ &= \hat{a}^\dagger(\hat{H} + \hbar\omega_0)|\psi_n\rangle \\ &= (E_n + \hbar\omega_0)\hat{a}^\dagger|\psi_n\rangle \end{aligned} \tag{4.12}$$

Conclusion:
If $|\psi_n\rangle$ is eigenvector of $\hat{H}$ to the eigenvalue E_n, then $|\psi_n^+\rangle := \hat{a}^\dagger|\psi_n\rangle$ is eigenvector to the eigenvalue $E_n + \hbar\omega_0$, and $|\psi_n^-\rangle := \hat{a}|\psi_n\rangle$ is eigenvector to the eigenvalue $E_n - \hbar\omega_0$.

If $|\psi\rangle$ is a normalized eigenvector of $\hat{H}$ $\Big(\langle\psi|\psi\rangle = 1\Big)$ to the eigenvalue E, then:

$$\begin{aligned} E &= \langle\psi|\hat{H}|\psi\rangle \;=\; \hbar\omega_0\langle\psi|\hat{a}^\dagger\hat{a} + \frac{1}{2}|\psi\rangle \\ &= \frac{\hbar\omega_0}{2} + \hbar\omega_0\langle\psi|\hat{a}^\dagger\hat{a}|\psi\rangle \\ &= \frac{\hbar\omega_0}{2} + \hbar\omega_0\langle\hat{a}\psi|\hat{a}\psi\rangle \\ \iff \quad E - \frac{\hbar\omega_0}{2} &= \hbar\omega_0\langle\psi^-|\psi^-\rangle \;\geq\; 0 \\ \iff \quad E &\geq \frac{\hbar\omega_0}{2} \end{aligned}$$

i.e. the spectrum is bounded from below.

Is $E = \frac{\hbar\omega_0}{2}$ possible? Yes!
proof by reductio ad absurdum

$$\begin{aligned} \text{assume :} \qquad E_0 &= \min\Big\{E_n\Big\} > \frac{\hbar\omega_0}{2} \\ \hookrightarrow \quad \frac{\hbar\omega_0}{2} &< E_0 = \langle\psi_0|\hat{H}|\psi_0\rangle = \frac{\hbar\omega_0}{2} + \hbar\omega_0\langle\hat{a}\psi_0|\hat{a}\psi_0\rangle \\ \Longleftrightarrow \quad 0 &< \langle\hat{a}\psi_0|\hat{a}\psi_0\rangle = \langle\psi_0^-|\psi_0^-\rangle \end{aligned}$$

$$\Longrightarrow \quad |\psi_0^-\rangle \text{ eigenvector of } \hat{H} \text{ to } E_0 - \frac{\hbar\omega_0}{2} \quad \text{contradiction!}$$

Conclusion: ground state $|\psi_0\rangle$ is eigenvector to the eigenvalue $E_0 = \frac{\hbar\omega_0}{2}$

$$\begin{aligned} \hookrightarrow \quad E_0 &= \langle\psi_0|\hat{H}|\psi_0\rangle \\ &= \frac{\hbar\omega_0}{2} + \hbar\omega_0\langle\hat{a}\psi_0|\hat{a}\psi_0\rangle \\ &= \frac{\hbar\omega_0}{2} \end{aligned}$$

$$\Longrightarrow \quad \boxed{\hat{a}|\psi_0\rangle = 0}$$

From (4.12) it follows that the first excited state has the eigenenergy $E_1 = E_0 + \hbar\omega_0 = \frac{3\hbar\omega_0}{2}$, the second $E_2 = E_1 + \hbar\omega_0 = \frac{5\hbar\omega_0}{2}$ etc.

$$\boxed{\begin{aligned} &\hookrightarrow \quad \text{eigenvalue spectrum of the harmonic oscillator} \\ &E_n = \hbar\omega_0\Big(n + \frac{1}{2}\Big) \,, \qquad n = 0, 1, 2, ... \end{aligned}} \tag{4.13}$$

c) Eigenstates

- the ground state is defined via

$$\hat{a}|\psi_0\rangle = 0 \,, \quad \langle\psi_0|\psi_0\rangle = 1 \tag{4.14}$$

- first excited state is generated by $|\psi_0^\dagger\rangle := \hat{a}^\dagger|\psi_0\rangle$

$$\begin{aligned} \hookrightarrow \quad \langle\psi_0^\dagger|\psi_0^\dagger\rangle &= \langle\psi_0|\hat{a}\hat{a}^\dagger|\psi_0\rangle \\ &= \langle\psi_0|\hat{a}^\dagger\hat{a}|\psi_0\rangle + \langle\psi_0|[\hat{a}, \hat{a}^\dagger]|\psi_0\rangle \\ &= \langle\psi_0|\psi_0\rangle = 1 \end{aligned}$$

$$\hookrightarrow \quad |\psi_1\rangle \equiv |\psi_0^\dagger\rangle \quad \text{is normalized eigenstate to } E_1$$

- second excited state $|\psi_1^\dagger\rangle := \hat{a}^\dagger|\psi_1\rangle$

$$\begin{aligned} \hookrightarrow \quad \langle\psi_1^\dagger|\psi_1^\dagger\rangle &= \langle\psi_1|\hat{a}\hat{a}^\dagger|\psi_1\rangle \\ &= \langle\psi_1|\hat{a}^\dagger\hat{a}|\psi_1\rangle + \langle\psi_1|[\hat{a},\hat{a}^\dagger]|\psi_1\rangle \\ &= \langle\psi_0|\psi_0\rangle + \langle\psi_1|\psi_1\rangle \;=\; 2 \end{aligned}$$

normalized eigenstate to $E_2 = \frac{5\hbar\omega_0}{2}$

$$\hookrightarrow \quad |\psi_2\rangle = \frac{1}{\sqrt{2}}\hat{a}^\dagger|\psi_1\rangle = \frac{1}{\sqrt{2}}\left(\hat{a}^\dagger\right)^2|\psi_0\rangle$$

In general: If $|\psi_n\rangle$ is the normalized eigenstate to E_n $\implies$ $|\psi_{n+1}\rangle = \frac{1}{\sqrt{n+1}}\hat{a}^\dagger|\psi_n\rangle$ is the normalized eigenstate to E_{n+1}

proof (of normalization):

$$\begin{aligned} \langle\psi_{n+1}|\psi_{n+1}\rangle &= \frac{1}{n+1}\langle\psi_n|\hat{a}\hat{a}^\dagger|\psi_n\rangle \\ &= \frac{1}{n+1}\left\{\frac{1}{\hbar\omega_0}\langle\psi_n|\hat{H}|\psi_n\rangle + \frac{1}{2}\right\} \\ &= \frac{1}{n+1}\left\{n+\frac{1}{2}+\frac{1}{2}\right\} \;=\; 1 \end{aligned}$$

Similarly, one can show that $|\psi_{n-1}\rangle = \frac{1}{\sqrt{n}}\hat{a}|\psi_n\rangle$ is the normalized eigenstate to E_{n-1}

Summary:

$$\boxed{|\psi_n\rangle = \tfrac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n|\psi_0\rangle \text{ is the normalized eigenstate to } E_n} \qquad (4.15)$$

4.1.2 Discussion

a) Coordinate space representation of the eigenvectors

Option 1) starting point: consider coordinate space representation of

$$\begin{aligned} \hat{a}|\psi_0\rangle &= 0 \\ &= \frac{1}{\sqrt{2m\hbar\omega_0}}(\hat{p} - im\omega_0\hat{x})|\psi_0\rangle \end{aligned}$$

$$\begin{aligned} \hookrightarrow \quad \langle x|\hat{p}|\psi_0\rangle - im\omega_0\langle x|\hat{x}|\psi_0\rangle &= 0 \\ \overset{\text{chap. 3.2.2}}{\iff} \quad -i\hbar\psi_0'(x) - im\omega_0 x\psi_0(x) &= 0 \end{aligned}$$

this differential equation has the (normalized) solution

$$\psi_0(x) = \Big[\frac{m\omega_0}{\hbar\pi}\Big]^{\frac{1}{4}} e^{-\frac{m\omega_0}{2\hbar}x^2} \tag{4.16}$$

excited states: $\langle x|\psi_n\rangle = \frac{1}{\sqrt{n!}}\langle x|(a^\dagger)^n|\psi_0\rangle$

$$\begin{aligned} \Longleftrightarrow \quad \psi_n(x) &= \frac{1}{\sqrt{n!}}\frac{1}{[2m\hbar\omega_0]^{\frac{n}{2}}}\Big(\frac{\hbar}{i}\frac{d}{dx} + im\omega_0 x\Big)^n \psi_0(x) \\ = \overset{\text{one can show:}}{\cdots} &= \Big[\frac{m\omega_0}{\hbar\pi}\Big]^{\frac{1}{4}}\sqrt{\frac{1}{2^n n!}} e^{-\frac{m\omega_0}{2\hbar}x^2} H_n\Big(\sqrt{\frac{m\omega_0}{\hbar}}x\Big) \end{aligned}$$

(Hermite's functions, see chapter 3.1.1)

Option 2) solve Schrödinger equation in position space

Literature: [Fli], chap. 12; [Gre], chap. 7; [DL], chap. 5.3

b) Properties of the eigensolutions

(i) Energy spectrum is discrete and equidistant

(ii) Zero-point energy $E_0 = \frac{\hbar\omega_0}{2} > 0 \quad \longleftrightarrow \quad$ uncertainty-relation (cf. chap. 2.4.2d)

one can show that for the $n-$th eigenstate:

$$\Delta x_n \Delta p_n = \frac{E_n}{\omega_0} = \hbar\Big(n + \frac{1}{2}\Big)$$

in particular $\Delta x_0 \Delta p_0 = \frac{\hbar}{2}$ (minimal uncertainty)

(iii) number of nodes + parity: same as for infinitely deep potential well (cf. chap. 2.4.2d)

c) Some special features

Literature: [Mes] I, chap. 12.2; [Scha], § 13

d) Meaning of the creation and annihilation operator

the creation operator enhances the excitation

$$\hat{a}^\dagger|\psi_n\rangle = \sqrt{n+1}|\psi_{n+1}\rangle \qquad\qquad E_n \overset{+\hbar\omega_0}{\longrightarrow} E_{n+1}$$

the annihilation operator reduces the excitation

$$\hat{a}|\psi_n\rangle = \sqrt{n}|\psi_{n-1}\rangle \qquad\qquad E_n \overset{-\hbar\omega_0}{\longrightarrow} E_{n-1}$$

- 'conventional' interpretation of the oscillator:
  one particle with mass m in ground or excited state with energy E_n
- 'field-quantum' interpretation:
  system consisting of n 'field-quanta' with the constant energy $\varepsilon = \hbar\omega_0$ in 'mode' ω_0

  $E_0 \;\hat{=}\;$ no 'particle' (but zero-point oscillation)
  $E_1 \;\hat{=}\;$ one 'particle'
  $\vdots$
  $E_n \;\hat{=}\;$ n 'particles'

  $\longrightarrow$ $\hat{a}$, $\hat{a}^\dagger$ create and annihilate these 'particles' (field-quanta)

  example: photons = field-quanta of the EM-field

e) Multi-dimensional and coupled oscillators

Literature: [Blöc], chap. 5.5.3; [Gre] I, chap. 14

4.2 Approximation methods

Only a few QM problems can be solved exactly. In most cases one has to resort to approximation techniques (or numerical methods or a combination of both). Here, we sketch only the most 'fundamental' approximation methods; perturbation theory and variational methods.

4.2.1 Stationary perturbation theory

Idea: Start with a simpler problem and use its known solution to construct an (approximate) solution of the problem at hand

a) Formulation

task: solve stationary Schrödinger Equation (i.e. $\partial_t \hat{H} = 0$)

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \tag{4.17}$$

decompose

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{4.18}$$

assume that $\hat{H}_0$ problem can be solved

$$\hat{H}_0|\psi_n^0\rangle = E_n^{(0)}|\psi_n^0\rangle \tag{4.19}$$

We'd like to seek solutions cf. eq. (4.17) in terms of a Taylor (like) expansion based on the eigenvalues and eigenstates of the 'undisturbed problem'

eq. (4.19). Therefore, we require that the 'perturbation' $\hat{V}$ be small. Let's introduce a parameter λ:

$$\hat{V} \equiv \lambda \hat{W} \qquad \text{with} \quad \lambda \ll 1 \tag{4.20}$$

$$\xrightarrow{(4.17)} \qquad \Big(\hat{H}_0 + \lambda \hat{W}\Big)|\psi_n(\lambda)\rangle = E_n(\lambda)|\psi_n(\lambda)\rangle \tag{4.21}$$

Taylor expansion about $\lambda = 0$:

$$E_n(\lambda) \;=\; E_n^{(0)} + \left.\frac{dE_n(\lambda)}{d\lambda}\right|_{\lambda=0} \lambda + \frac{1}{2}\frac{d^2E_n(\lambda)}{d\lambda^2}\lambda^2 + \ldots \tag{4.22}$$

$$|\psi_n(\lambda)\rangle \;=\; |\psi_n^0\rangle + \frac{d}{d\lambda}\,|\psi_n(\lambda)\rangle|_{\lambda=0}\,\lambda + \ldots \tag{4.23}$$

We need to find expressions for the derivatives in eqs. (4.22), (4.23): consider derivative cf. eq. (4.21):

$$\begin{aligned}
&\frac{d}{d\lambda}\Big(\hat{H}_0 + \lambda\hat{W} - E_n(\lambda)\Big)|\psi_n(\lambda)\rangle = 0 \\
\Longleftrightarrow\quad &\Big(\hat{H}_0 + \lambda\hat{W} - E_n(\lambda)\Big)|\psi_n'(\lambda)\rangle + \Big(\hat{W} - E_n'(\lambda)\Big)|\psi_n(\lambda)\rangle = 0 \\
&\qquad (E_n' = \frac{dE_n}{d\lambda} \quad \text{etc.}) \\
\hookrightarrow\quad &\langle\psi_m(\lambda)|\hat{H}(\lambda) - E_n(\lambda)|\psi_n'(\lambda)\rangle + \langle\psi_m(\lambda)|\hat{W} - E_n'(\lambda)|\psi_n(\lambda)\rangle = 0
\end{aligned}$$

i) $m = n$

$$\Longrightarrow \quad E_n'(\lambda) = \langle\psi_n(\lambda)|\hat{W}|\psi_n(\lambda)\rangle \tag{4.24}$$

ii) $m \neq n$

$$\Longrightarrow \quad \langle\psi_m(\lambda)|\psi_n'(\lambda)\rangle = \frac{\langle\psi_m(\lambda)|\hat{W}|\psi_n(\lambda)\rangle}{E_n(\lambda) - E_m(\lambda)} \tag{4.25}$$

In order to use eq. (4.25) for an expansion of $|\psi_n'\rangle$ in terms of the orthonormal basis $\big\{|\psi_n\rangle\big\}$ we have to consider the coefficient $\langle\psi_n(\lambda)|\psi_n'(\lambda)\rangle$ in addition. If we assume that $\langle\psi_n(\lambda)|\psi_n'(\lambda)\rangle = \langle\psi_n'(\lambda)|\psi_n(\lambda)\rangle$ (i.e. we choose real states which is not a restriction) we can show that

$$\langle\psi_n(\lambda)|\psi_n'(\lambda)\rangle = 0$$

proof :

$$\begin{aligned}
\frac{d}{d\lambda}\underbrace{\langle\psi_n(\lambda)|\psi_n(\lambda)\rangle}_{=1} \;&=\; \langle\psi_n'(\lambda)|\psi_n(\lambda)\rangle + \langle\psi_n(\lambda)|\psi_n'(\lambda)\rangle \\
&=\; 2\langle\psi_n(\lambda)|\psi_n'(\lambda)\rangle \;=\; 0
\end{aligned}$$

$$\hookrightarrow \quad |\psi_n'(\lambda)\rangle = \sum_m |\psi_m(\lambda)\rangle\langle\psi_m(\lambda)|\psi_n'(\lambda)\rangle$$
$$= \sum_{m\neq n} \frac{\langle\psi_m(\lambda)|\hat{W}|\psi_n(\lambda)\rangle}{E_n(\lambda)-E_m(\lambda)}|\psi_m(\lambda)\rangle \tag{4.26}$$

We consider also the 2^{nd} derivative term in eq. (4.22):

$$\frac{d^2}{d\lambda^2}E_n(\lambda) = \frac{d}{d\lambda}E_n'(\lambda) \overset{(4.24)}{=} \frac{d}{d\lambda}\langle\psi_n(\lambda)|\hat{W}|\psi_n(\lambda)\rangle$$
$$= \langle\psi_n'(\lambda)|\hat{W}|\psi_n(\lambda)\rangle + \langle\psi_n(\lambda)|\hat{W}|\psi_n'(\lambda)\rangle$$
$$\overset{(4.26)}{=} 2\sum_{m\neq n}\frac{|\langle\psi_n(\lambda)|\hat{W}|\psi_m(\lambda)\rangle|^2}{E_n(\lambda)-E_m(\lambda)} \tag{4.27}$$

Higher order terms can be calculated by differentiating expressions (4.26), (4.27) successively. We stop here and insert (4.24)-(4.27) in the Taylor expansions (4.22), (4.23):

$$E_n(\lambda) = E_n^{(0)} + \lambda\langle\psi_n(0)|\hat{W}|\psi_n(0)\rangle + \lambda^2\sum_{m\neq n}\frac{|\langle\psi_n(0)|\hat{W}|\psi_m(0)\rangle|^2}{E_n(0)-E_m(0)} + \ldots \tag{4.28}$$
$$= E_n^{(0)} + \langle\psi_n^0|\hat{V}|\psi_n^0\rangle + \sum_{m\neq n}\frac{|\langle\psi_n^0|\hat{V}|\psi_m^0\rangle|^2}{E_n^{(0)}-E_m^{(0)}} + \ldots$$
$$|\psi_n(\lambda)\rangle = |\psi_n^0\rangle + \sum_{m\neq n}\frac{\langle\psi_m^0|\hat{V}|\psi_n^0\rangle}{E_n^{(0)}-E_m^{(0)}}|\psi_m^0\rangle + \ldots \tag{4.29}$$

eqs. (4.28), (4.29) are the standard expressions for the lowest-order corrections.

b) Remarks:

1. Derivation and result are valid only if $E_n^{(0)} \neq E_m^{(0)}$ (i.e. no degeneracies) For degenerate perturbation theory $\longrightarrow$ QM literature, e.g. [Jel], chap. 7
2. Convergence of perturbation series?
   Cannot be answered in general. In some cases, perturbation expansions do converge, in some they do not, and in some other cases the

perturbation series turns out to be a so-called semi-convergent (asymptotic) series.

Consistency criterion for convergence (check eq. (4.29))

$$\left| \frac{\langle \psi_m^0 | \hat{V} | \psi_n^0 \rangle}{E_n^{(0)} - E_m^{(0)}} \right| \ll 1 \ , \qquad (\text{for } n \neq m)$$

further reading: e.g. [Jel], chap. 7.2

3. In practice, 'exact' calculations beyond 1^{st} order are often not feasible due to (infinite) sums over all basis states (cf. eq. (4.29)).
4. Variants of stationary perturbation theory (as well as more formal derivations) exist.
   Literature: [Jel], chap. 9; [Mes], QM II, chap. 16; [DL], chap. 11

c) Example: Perturbed harmonic oscillator (1-d)

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{m}{2}\omega_0^2 x^2 \tag{4.30}$$

$\longrightarrow$ can be solved exactly (chap. 4.1)

1. linear perturbation

$$\hat{V} = ax \ , \qquad (a \ \in \ \mathbb{R}) \tag{4.31}$$

We need - cf. eq. (4.29) - matrix elements

$$\langle \psi_n^0 | \hat{V} | \psi_m^0 \rangle = a \langle \psi_n^0 | \hat{x} | \psi_m^0 \rangle$$

$\longrightarrow$ can be calculated e.g. by using (well-known and easy-to-prove) recursion relations for Hermite's polynomials and functions

$$\sqrt{\lambda} x \psi_n^0(x) \ = \ \sqrt{\frac{n+1}{2}} \psi_{n+1}^0(x) + \sqrt{\frac{n}{2}} \psi_{n-1}^0(x)$$

$$\hookrightarrow \quad \langle \psi_n^0 | \hat{x} | \psi_m^0 \rangle \ = \ \sqrt{\frac{\hbar}{m\omega_0}} \left\{ \sqrt{\frac{n+1}{2}} \delta_{n+1,m} + \sqrt{\frac{n}{2}} \delta_{n-1,m} \right\}$$

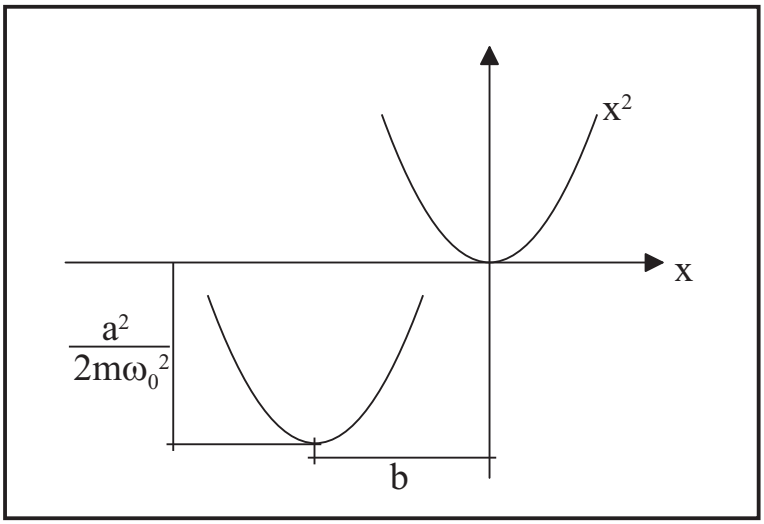
$\longrightarrow$ i.e. almost all matrix elements vanish!
to 2^{nd} order:

$$\begin{aligned} E_n \ &\approx \ E_n^{(0)} + E_n^{(1)} + E_n^{(2)} \\ &= \ \hbar\omega_0 (n + \frac{1}{2}) + 0 + \Big(- \frac{a^2}{2m\omega_0^2} \Big) \end{aligned} \tag{4.32}$$

It turns out, that all higher-order terms vanish and eq. (4.32) is the exakt solution! This can be seen from a different viewpoint:

$$\begin{aligned}\hat{H} &= \hat{H}_0 + \hat{V} = \frac{\hat{p}^2}{2m} + \frac{m}{2}\omega_0^2 x^2 + ax \\ &= \frac{\hat{p}^2}{2m} + \frac{m}{2}\omega_0^2 (x+b)^2 - \frac{m}{2}\omega_0^2 b^2 \\ &\qquad (\text{with} \quad a = m\omega_0^2 b)\end{aligned}$$

$\longrightarrow$ the oscillator potential is not really disturbed, but only displaced!



$\longrightarrow$ all eigenenergies are shifted by $-\frac{m}{2}\omega_0^2 b^2 = -\frac{a^2}{2m\omega_0^2}$!

2. Anharmonic oscillator

$$\hat{V} = c\hat{x}^3 \tag{4.33}$$

i.e., calculate matrix elements $\langle \psi_n^0 | x^3 | \psi_m^0 \rangle$. In this case, the 1^{st} order energy correction vanishes as well, but higher orders do contribute.

Further discussion of undisturbed and disturbed harmonic oscillator: [CT] I, chap. 5 and II, chap. 11.4

4.2.2 Variational methods

a) Rayleigh-Ritz principle (of minimal energy)

Consider energy functional (functional=linear map vector $\longmapsto$ scalar)

$$E[\phi] = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \tag{4.34}$$

The expectation value of $\hat{H}$ with respect to any trial state $|\phi\rangle$ is larger than (or equal to) the true groundstate energy, i.e., the lowest eigenvalue of $\hat{H}$

proof :

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

with

$$\langle\psi_n|\psi_k\rangle = \delta_{nk}$$

and

$$\sum_n |\psi_n\rangle\langle\psi_n| = \hat{1}$$

We can expand each trial function:

$$|\phi\rangle = \sum_j c_j|\psi_j\rangle$$

consider

$$\begin{aligned}\Delta E &\equiv E[\phi] - E_0 \\ &= \frac{\langle\phi|\hat{H} - E_0|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\sum_{jk} c_j^* c_k \langle\psi_j|\hat{H} - E_0|\psi_k\rangle}{\sum_j |c_j|^2} \\ &= \frac{\sum_j |c_j|^2 (E_j - E_0)}{\sum_j |c_j|^2} \begin{cases} = 0 & \text{if } |\phi\rangle = |\psi_0\rangle \\ > 0 & \text{otherwise} \end{cases}\end{aligned}$$

$\longrightarrow$ energy functional $E[\phi]$ is bounded by ground-state energy.

One exploits this principle in the following way:

- Choose a set of trial states $|\phi\rangle$
- Find the minimum of $E[\phi]$
- According to the Rayleigh-Ritz principle the state that minimizes the energy is the best approximation within the set!

b) Simple application

- consider $|\phi\rangle = |\phi(\lambda)\rangle$

$$\hookrightarrow \quad E[\phi] = \frac{\langle\phi(\lambda)|\hat{H}|\phi(\lambda)\rangle}{\langle\phi(\lambda)|\phi(\lambda)\rangle} = E(\lambda)$$

- search for minimum; i.e., calculate $\frac{dE(\lambda)}{d\lambda} = 0$

example: 1-dim harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m} d_x^2 + \frac{m}{2}\omega_0^2 x^2$$

$$\text{Ansatz :} \qquad \phi(x,\lambda) = A e^{-\frac{\lambda^2}{2}x^2}$$

$$\hookrightarrow \quad E(\lambda) = \frac{|A|^2 \int_{-\infty}^{\infty} e^{-\frac{\lambda^2}{2}x^2} \Big\{ -\frac{\hbar^2}{2m} d_x^2 + \frac{m}{2}\omega_0^2 x^2 \Big\} e^{-\frac{\lambda^2}{2}x^2}\, dx}{|A|^2 \int_{-\infty}^{\infty} e^{-\lambda^2 x^2}\, dx}$$

$$= \ldots = \frac{\hbar^2\lambda^2}{4m} + \frac{m\omega_0^2}{4\lambda^2}$$

$$\hookrightarrow \quad \frac{dE}{d\lambda} = \frac{\hbar^2\lambda}{2m} - \frac{m\omega_0^2}{2\lambda^3} = 0 \qquad \Longleftrightarrow \quad \lambda_0^2 = \frac{m\omega_0}{\hbar}$$

$$\hookrightarrow \quad \phi(x,\lambda_0) = A \exp\Big[-\frac{m\omega_0}{2\hbar} x^2 \Big] \qquad \text{(cf. eq. (4.16))}$$

$$E(\lambda_0) = \frac{1}{2\lambda_0^2}\Big[\frac{\hbar^2\lambda_0^4}{2m} + \frac{m\omega_0^2}{2} \Big] = \frac{\hbar\omega_0}{2}$$

$\hookrightarrow$ in fact, this is the true ground-state wave function (and energy).

One can refine the method by introducing trial wave functions that depend on more than one parameter or by considering other ansätze, such as the expansion of trial wave functions with respect to known finite basis systems, etc.

In fact, the variational method may be considered as the most important approximation technique for the determination of ground states.

4.2.3 Time-dependent perturbation theory

a) Formulation

task: solve TDSE (i.e. $\partial_t \hat{H} \neq 0$)

$$i\hbar\partial_t |\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle \tag{4.35}$$

decompose Hamiltonian (cf. eq. (4.18))

$$\begin{aligned} \hat{H}(t) &= \hat{H}_0 + \hat{V}(t) \\ &\equiv \hat{H}_0 + \lambda\hat{W}(t) \end{aligned} \tag{4.36}$$

assume that $\hat{W}(t \leq t_0) = 0$

$$\begin{aligned} \hookrightarrow \quad t \leq t_0: \qquad & \hat{H}_0|\varphi_j\rangle &&= \epsilon_j|\varphi_j\rangle \\ \text{assume} \qquad & |\psi(t_0)\rangle &&= |\varphi_0\rangle\,, \qquad \text{(initial state)} \end{aligned} \tag{4.37}$$

$$\begin{aligned} \text{Ansatz}: \qquad |\psi(t)\rangle &= \sum_j c_j(t) e^{-\frac{i}{\hbar}\epsilon_j t}|\varphi_j\rangle \\ &= \sum_j c_j(t)|\psi_j(t)\rangle \end{aligned} \tag{4.38}$$

Insertion cf. eq. (4.38) into eq. (4.35):

$$\hookrightarrow \quad \sum_j \Big(i\hbar\dot{c}_j + \epsilon_j\Big) e^{-\frac{i}{\hbar}\epsilon_j t}|\varphi_j\rangle = \sum_j c_j e^{-\frac{i}{\hbar}\epsilon_j t}\hat{H}|\varphi_j\rangle \qquad | \ \langle\psi_k(t)|$$

$$\hookrightarrow \quad i\hbar\dot{c}_k = \lambda \sum_j e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} c_j \langle\varphi_k|\hat{W}(t)|\varphi_j\rangle \tag{4.39}$$

'coupled-channel' eqs. (still exact if basis is complete)

If $\hat{W}(t > T) = 0 \qquad \hookrightarrow \quad c_k(t > T) = \text{const.}$ and

$$p_k = |c_k|^2\Big|_{t>T} = |\langle\varphi_k|\psi\rangle|^2\Big|_{t>T} = \text{const.} \tag{4.40}$$

$$\longrightarrow \text{transition probabilities } \varphi_0 \longrightarrow \varphi_k$$

Ansatz for solution of eq. (4.39):

$$c_k(t) = c_k^{(0)}(t) + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \ldots \tag{4.41}$$

Insertion into eq. (4.39) yields:

$$\begin{aligned} & i\hbar\Big(\dot{c}_k^{(0)} + \lambda\dot{c}_k^{(1)} + \lambda^2\dot{c}_k^{(2)} + \ldots\Big) \\ & \qquad = \lambda \sum_j \Big(c_j^{(0)} + \lambda c_j^{(1)} + \lambda^2 c_j^{(2)} + \ldots\Big) e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} \langle\varphi_k|\hat{W}(t)|\varphi_j\rangle \end{aligned}$$

$\hookrightarrow$

$$\begin{aligned} \lambda^0: \qquad & i\hbar\dot{c}_k^{(0)} = 0 \qquad \hookrightarrow \quad c_k^{(0)}(t) = \text{const.} \\ \lambda^1: \qquad & i\hbar\dot{c}_k^{(1)} = \sum_j c_j^{(0)} e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} \langle\varphi_k|\hat{W}(t)|\varphi_j\rangle \\ \lambda^2: \qquad & i\hbar\dot{c}_k^{(2)} = \sum_j c_j^{(1)} e^{\frac{i}{\hbar}(\epsilon_k - \epsilon_j)t} \langle\varphi_k|\hat{W}(t)|\varphi_j\rangle \end{aligned}$$

These equation can be solved successively:

$$\begin{aligned}
\lambda^0: \qquad c_k^{(0)}(t) &= \text{const.} = \delta_{k0} \qquad \text{(cf. eq. (4.37))} \qquad (4.42)\\
\lambda^1: \qquad i\hbar\dot{c}_k^{(1)} &= \sum_j \delta_{j0} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t}\langle\varphi_k|\hat{W}(t)|\varphi_j\rangle \\
&= e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t}\langle\varphi_k|\hat{W}(t)|\varphi_0\rangle
\end{aligned}$$

$$\hookrightarrow \quad c_k^{(1)}(t) - \underbrace{c_k^{(1)}(t_0)}_{=0} = -\frac{i}{\hbar}\int_{t_0}^{t} e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_0)t'}\langle\varphi_k|\hat{W}(t')|\varphi_0\rangle\, dt' \qquad (4.43)$$

(as $\lambda = 0$ at $t = t_0$)

Accordingly:

$$\begin{aligned}
\lambda^2: \qquad c_k^{(2)}(t) = -\frac{1}{\hbar^2}\sum_j \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{\frac{i}{\hbar}(\epsilon_k-\epsilon_j)t'} e^{\frac{i}{\hbar}(\epsilon_j-\epsilon_0)t''} \\
\times \langle\varphi_k|\hat{W}(t')|\varphi_j\rangle\langle\varphi_j|\hat{W}(t'')|\varphi_0\rangle \qquad (4.44)
\end{aligned}$$

(...)

Remarks:

(a) "Exakt" calculations beyond 1^{st} order are in general impossible due to infinite sums (cf. page 105)

(b) Interpretation

	t_0			t	
1^{st} order	$\|\varphi_0\rangle$	$\xrightarrow{\hat{W}}$		$\|\varphi_k\rangle$	'direct transition'
2^{nd} order	$\|\varphi_0\rangle$	$\xrightarrow{\hat{W}}$	$\|\varphi_j\rangle$ $\xrightarrow{\hat{W}}$	$\|\varphi_k\rangle$	

transition via 'virtual' intermediate states (2 steps)

further reading (and more appropriate 'visualization' in terms of generic diagrams): [Mes], QM II, chap. 17

b) Discussion of 1^{st} order $\longrightarrow$ Fermi's Golden Rule (FGR)

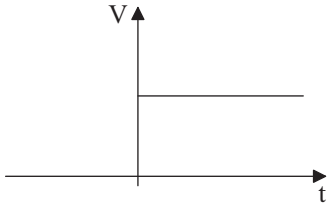
To 1^{st} order time-dependent perturbation theory we have (cf. eq. (4.42), (4.43)):

$$c_k(t) \approx \delta_{k0} - \frac{i}{\hbar}\int_{t_0}^{t} e^{i\omega_{k0}t'} V_{k0}(t')\, dt' \qquad (4.45)$$

$$\begin{aligned}
\text{with} \qquad \omega_{k0} &= \omega_k - \omega_0 = \frac{\epsilon_k - \epsilon_0}{\hbar} \qquad \text{'transition frequency'} \\
V_{k0} &= \langle\varphi_k|\hat{V}|\varphi_0\rangle = \lambda\langle\varphi_k|\hat{W}|\varphi_0\rangle \\
&\quad \text{'transition matrix element'}
\end{aligned}$$

Two useful (and related) examples:

(i) Sudden perturbation (somewhat academic)



$$\hat{V}(t) = \begin{cases} 0 & t \leq t_0 \equiv 0 \\ \hat{V} & t > t_0 \end{cases}$$

$\boxed{k \neq 0}$

$$\begin{aligned} \hookrightarrow \quad c_k(t) &= -\frac{i}{\hbar}\int_0^t e^{i\omega_{k0}t'} V_{k0}(t')\, dt' \\ &= \frac{\langle\varphi_k|\hat{V}|\varphi_0\rangle}{i\hbar}\int_0^t e^{i\omega_{k0}t'}\, dt' \\ &= -\frac{\langle\varphi_k|\hat{V}|\varphi_0\rangle}{\hbar\omega_{k0}}\Big(e^{i\omega_{k0}t} - 1\Big) \end{aligned}$$

$\hookrightarrow$ transition probability

$$p_{0\to k}(t) = |c_k(t)|^2 = \frac{4|V_{k0}|^2}{\hbar^2} f(t,\omega_{k0}) \tag{4.46}$$

$$f(t,\omega_{k0}) = \frac{\sin^2\frac{\omega_{k0}t}{2}}{\omega_{k0}^2} \xrightarrow{\omega_{k0}\to 0} \frac{t^2}{4} \tag{4.47}$$

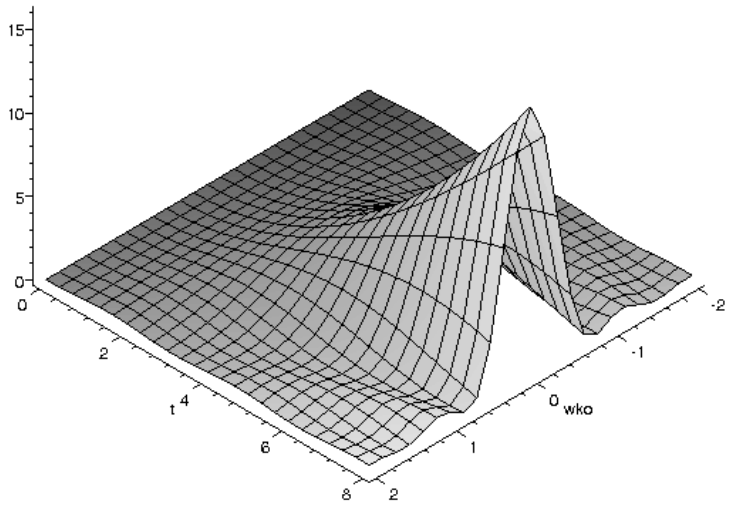


Figure 4.1: $y = f(t,\omega_{k0})$

significant transitions occur only around $\omega_{k0} = 0$ within width $\Delta\omega = \frac{2\pi}{t}$

One can consider limit $t \longrightarrow \infty$:

$$f(t, \omega_{k0}) \quad \stackrel{t\to\infty}{\longrightarrow} \quad \frac{\pi t}{2}\delta(\omega_k - \omega_0) \tag{4.48}$$

$$\hookrightarrow \quad p_{0\to k} \quad \stackrel{t\to\infty}{\longrightarrow} \quad \frac{2\pi t}{\hbar}|V_{k0}|^2\delta(\omega_k - \omega_0)$$

(ii) Periodic perturbation

$$\hat{V}(t) = \begin{cases} 0 & t \le t_0 = 0 \\ \hat{B}e^{i\omega t} + \hat{B}^\dagger e^{-i\omega t} & t > t_0 \end{cases} \tag{4.49}$$

(note that $\hat{V} = \hat{V}^\dagger$)

$$\begin{aligned} \hookrightarrow \quad c_k(t) &= \frac{1}{i\hbar}\int_0^t e^{i\omega_{k0}t'}V_{k0}(t')\,dt' \\ &= -\frac{1}{\hbar}\Bigg\{\frac{\langle\varphi_k|\hat{B}|\varphi_0\rangle}{\omega_{k0}+\omega}\Big(e^{i(\omega_{k0}+\omega)t} - 1\Big) \\ &\qquad + \frac{\langle\varphi_k|\hat{B}^\dagger|\varphi_0\rangle}{\omega_{k0}-\omega}\Big(e^{i(\omega_{k0}-\omega)t} - 1\Big)\Bigg\} \end{aligned}$$

if $t \gg \frac{2\pi}{\omega}$ (i.e. $\Delta\omega \ll \omega$):

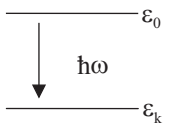
$$p_{0\to k}(t) = \frac{4|B_{k0}|^2}{\hbar^2}\Big\{f(t, \omega_{k0}+\omega) + f(t, \omega_{k0}-\omega)\Big\} \tag{4.50}$$

$$\stackrel{t\to\infty}{\longrightarrow} \quad \frac{2\pi t}{\hbar}|B_{k0}|^2\Big\{\delta(\omega_k - \omega_0 + \omega) + \delta(\omega_k - \omega_0 - \omega)\Big\}$$

with $B_{k0} = \langle\varphi_k|\hat{B}|\varphi_0\rangle$ and eq. (4.47)

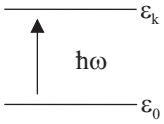
'resonances' at $\omega_{k0} = \pm\omega$ (significant transitions occur only around these resonance frequencies)

- $\omega_{k0} = -\omega \quad \Longleftrightarrow \quad \epsilon_k = \epsilon_0 - \hbar\omega$



'stimulated emission' (of energy)
(only possible if φ_0 is not the ground state)

- $\omega_{k0} = +\omega \quad \Longleftrightarrow \quad \epsilon_k = \epsilon_0 + \hbar\omega$



(stimulated) absorbtion (of energy)

If one considers a quantum particle in a (weak) classical electromagnetic (EM) field (eq. (2.52)) one can rewrite the Hamiltonian such that it takes the form $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$ with eq. (4.49) for $\hat{V}$. One can interpret the stimulated emission of the energy 'packet' $\hbar\omega$ as the emission of a photon with energy $\hbar\omega$ and the absorption of $\hbar\omega$ as the absorption of a photon from the radiation field. The latter process corresponds to the photoelectric effect (cf. page 2) if the final state is a (true) continuum state (i.e., if an electron is ionized).

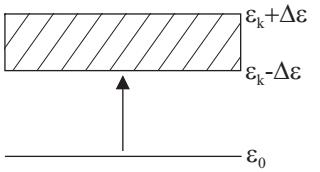
problems:

(i) $p_{0\to k} \longrightarrow \infty$ for $t \to \infty$ and $\omega_{k0} \to \pm\omega$

(ii) $p_{0\to k}(t)$ oscillates (is proportional to t^2 for $\omega_{k0} = \pm\omega$)

$\hookrightarrow$ (i) and (ii) seem unphysical!

solution: consider transitions into continuum of final states
(it turns out that this is always justified for realistic systems due to finite line-width of excited states)



$$P_{0\to k,\Delta k} = \int_{\epsilon_k-\Delta\epsilon}^{\epsilon_k+\Delta\epsilon} p_{0\to k}(\epsilon'_k)\rho(\epsilon'_k)\, d\epsilon'_k \quad (4.51)$$

with $\rho(\epsilon_k)$: density of states $\Big($in interval $[\epsilon_k - \Delta\epsilon; \epsilon_k + \Delta\epsilon]\Big)$

One finds with eqs. (4.48) - (4.50)

$$\begin{aligned} P_{0\to k,\Delta k} &= \frac{2\pi t}{\hbar^2} \int |B_{k0}|^2 \rho(\epsilon'_k) \Big\{ \delta(\omega_k - \omega_0 + \omega) + \delta(\omega_k - \omega_0 - \omega) \Big\} d(\hbar\omega'_k) \\ &= \frac{2\pi}{\hbar} \Big\{ |B_{k0}|^2 \rho(\epsilon_k) t \Big|_{\epsilon_k - \epsilon_0 = \hbar\omega} + |B_{k0}|^2 \rho(\epsilon_k) t \Big|_{\epsilon_0 - \epsilon_k = \hbar\omega} \Big\} \end{aligned}$$

define transition rate $w_{0\to k,\Delta k} = \frac{d}{dt} P_{0\to k,\Delta k}$

$\longrightarrow$ Fermi's Golden Rule (FGR)

$$\hookrightarrow \quad w_{0 \overset{\text{emission}}{\longrightarrow} k,\Delta k} = w_{0 \overset{\text{absorption}}{\longrightarrow} k,\Delta k} = \frac{2\pi}{\hbar}|B_{k0}|^2 \rho(\epsilon_k)\Big|_{\epsilon_k=\epsilon_0\pm\hbar\omega} \tag{4.52}$$

Note that $w_{0\to k,\Delta k}$ is constant (i.e. does not depend on t).
For actual calculations three ingredients are needed (see App. A.2):

1) Explicit form of $\hat{B}$
   starting point: Hamiltonian for a particle in the EM field (eq. (2.73))
2) Initial and final states to calculate B_{k0}
3) Density of states $\rho(\epsilon_k)$

Literature: [Scha], chap. 11; [BS], chap. IV

Note that the notion of photons for the interpretation of stimulated emission and absorbtion has no significance as long as we are dealing with classical EM fields. From a theoretical point of view photons enter the game only if the EM field is 'quantized' ($\longrightarrow$ quantum electrodynamics (QED)). This quantization does not change the final expressions for stimulated emission and absorbtion, but it shows that there is another process which cannot be described in our 'semiclassical' framework: spontaneous emission, i.e., the emission of a photon (and transition to a lower-lying state) without any external EM field.

A relatively simple account on the quantization of the EM field can be found, e.g., in: [Fri], chap. 2.4 or [**?**], chap. 1-2
'higher formulations': [Scha], chap. 14; [Mes], chap. 21 (and of course, QED textbooks)

4.3 Angular momentum and spin

- We have introduced 'orbital angular momentum' of a particle by (eq. (3.81))

$$\hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$$

consequences:
- $\hat{l}_x, \hat{l}_y, \hat{l}_z$ hermitian
- $[\hat{l}_i, \hat{l}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{l}_k$

- Turn the argument upside-down and define a 'general' angular momentum operator $\hat{\mathbf{J}}$ as a vector operator:

$$\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$$

with hermitian components which satisfy

$$[\hat{J}_i, \hat{J}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{J}_k \tag{4.53}$$

All properties of angular momentum in QM follow from this definition.

4.3.1 Angular momentum algebra

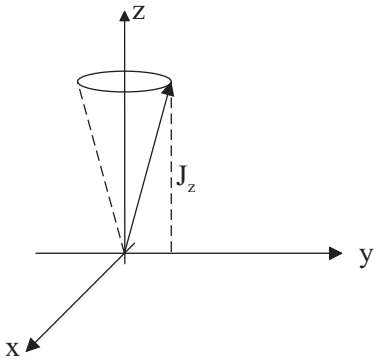
Definition:

$$\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \tag{4.54}$$

$$\hookrightarrow \quad [\hat{\mathbf{J}}^2, \hat{J}_i] = 0 \ , \quad (i = 1, 2, 3) \tag{4.55}$$

proof:

$$\begin{aligned} [\hat{\mathbf{J}}^2, \hat{J}_z] &= [\hat{J}_x^2 + \hat{J}_y^2, \hat{J}_z] \\ &= [\hat{J}_x, \hat{J}_z]\hat{J}_x + \hat{J}_x[\hat{J}_x, \hat{J}_z] + [\hat{J}_y, \hat{J}_z]\hat{J}_y + \hat{J}_y[\hat{J}_y, \hat{J}_z] \\ &= \frac{\hbar}{i}\Big\{ \hat{J}_y\hat{J}_x + \hat{J}_x\hat{J}_y - \hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x \Big\} \ = \ 0 \quad \text{etc.} \end{aligned}$$



$\longrightarrow$ one component can be measured simultaneously with the absolute square. Usually, one picks the z-component.

- Eigenvalue problems of $\hat{\mathbf{J}}^2, \hat{J}_z$:

$$\hat{\mathbf{J}}^2|\varphi_{jm}\rangle = \lambda_j|\varphi_{jm}\rangle \tag{4.56}$$

$$\hat{J}_z|\varphi_{jm}\rangle = \mu_m|\varphi_{jm}\rangle \tag{4.57}$$

We abbreviate the common eigenstates by their quantum numbers:

$$|\varphi_{jm}\rangle \ \longrightarrow \ |jm\rangle \ , \quad (\ \langle jm|j'm'\rangle = \delta_{jj'}\delta_{mm'} \ )$$

What can we say about the eigenvalues $\lambda_j, \ \mu_m$?

$\lhd$ $\qquad \langle\psi|\hat{J}_i^2|\psi\rangle \overset{\hat{J}_i=\hat{J}_i^\dagger}{=} \langle\hat{J}_i\psi|\hat{J}_i\psi\rangle \geq 0 \ , \qquad (\ \forall \ |\psi\rangle \ )$

in particular:

$$\langle jm|\hat{\mathbf{J}}^2|jm\rangle = \boxed{\lambda_j \geq 0} \tag{4.58}$$

$$\begin{aligned}\langle jm|\hat{J}_x^2 + \hat{J}_y^2|jm\rangle &= \langle jm|\hat{\mathbf{J}}^2 - \hat{J}_z^2|jm\rangle \\ &= \lambda_j - \mu_m^2 \;\geq\; 0\end{aligned}$$

$$\boxed{\hookrightarrow \qquad -\sqrt{\lambda_j} \;\leq\; \mu_m \;\leq\; \sqrt{\lambda_j}} \tag{4.59}$$

(i.e. spectrum of $\hat{J}_z$ is bounded by eigenvalues of $\hat{\mathbf{J}}^2$!)

define 'ladder operators' (cf. creation and annihilation operators in chap. 4.1)

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y \tag{4.60}$$

$$\hat{J}_- = \hat{J}_x - i\hat{J}_y \tag{4.61}$$

$$\hookrightarrow \quad \hat{J}_+^\dagger = \hat{J}_- \,, \quad \hat{J}_-^\dagger = \hat{J}_+ \tag{4.62}$$

Some useful relations (easy to prove):

$$[\hat{J}_z, \hat{J}_\pm] = \pm\hbar\hat{J}_\pm \tag{4.63}$$

$$[\hat{J}_z, \hat{J}_\pm^n] = \pm n\hbar\hat{J}_\pm^n \tag{4.64}$$

$$\hat{J}_-\hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z \;\searrow \qquad [\hat{J}_+, \hat{J}_-] = 2\hbar\hat{J}_z \tag{4.65}$$

$$\hat{J}_+\hat{J}_- = \hat{\mathbf{J}}^2 - \hat{J}_z^2 + \hbar\hat{J}_z \;\nearrow \tag{4.66}$$

$$[\hat{\mathbf{J}}^2, \hat{J}_\pm] = 0 \tag{4.67}$$

let's play with them:

$$\begin{aligned}\hat{J}_z\hat{J}_+|jm\rangle &\overset{(4.63)}{=} (\hat{J}_+\hat{J}_z + \hbar\hat{J}_+)|jm\rangle \\ &= (\mu_m + \hbar)\hat{J}_+|jm\rangle\end{aligned} \tag{4.68}$$

$$\left.\begin{array}{ll}\hookrightarrow & \hat{J}_+|jm\rangle = \alpha|jm'\rangle \\ \text{with} & \hat{J}_z|jm'\rangle = (\mu_m + \hbar)|jm'\rangle\end{array}\right\} \quad \begin{array}{l}\hat{J}_+|jm\rangle \text{ is another} \\ \text{eigenvector of } \hat{J}_z \text{ with} \\ \text{eigenvalue raised by } \hbar\end{array}$$

Norm of the eigenvector $\hat{J}_+|jm\rangle$:

$$\begin{aligned}||\hat{J}_+|jm\rangle||^2 &= \langle jm|\hat{J}_-\hat{J}_+|jm\rangle \overset{(4.65)}{=} \langle jm|\hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z|jm\rangle \\ &= \lambda_j - \mu_m^2 - \hbar\mu_m \;=\; |\alpha|^2\end{aligned}$$

There is one case where $||\hat{J}_+|jm\rangle||^2 = 0$; namely when

$$\begin{aligned} & \lambda_j - \mu_m^2 - \hbar\mu_m = 0 \\ \Longleftrightarrow \quad & \lambda_j = \mu_m(\mu_m + \hbar) \end{aligned}$$

On the other hand we know that the spectrum of $\hat{J}_z$ is bounded, i.e., there is a smallest and a largest eigenvalue (μ_{min}, μ_{max}). In particular, the eigenvalue eq.

$$\hat{J}_z|jm_{max}\rangle = \mu_{max}|jm_{max}\rangle$$

exists. Let's apply $\hat{J}_+$ to $|jm_{max}\rangle$:

$$\hookrightarrow \quad \hat{J}_+|jm_{max}\rangle = ?$$

$\longrightarrow$ it cannot raise eigenvalue by $\hbar$ as μ_{max} is already the largest eigenvalue. The only way out is

$$\hat{J}_+|jm_{max}\rangle = 0$$

which implies (see above)

$$\boxed{\lambda_j = \mu_{max}(\mu_{max} + \hbar)} \tag{4.69}$$

We can play the same game with $\hat{J}_-$:

$$\begin{aligned} \hookrightarrow \quad \hat{J}_-\hat{J}_z|jm\rangle \quad &\overset{(4.63)}{=} \quad (\mu_m - \hbar)\hat{J}_-|jm\rangle \\ ||\hat{J}_-|jm\rangle||^2 \quad &= \quad \langle jm|\hat{J}_+\hat{J}_-|jm\rangle \quad \overset{(4.66)}{=} \quad \lambda_j - \mu_m^2 + \hbar\mu_m \end{aligned}$$

There is a smallest eigenvalue μ_{min}

$$\hookrightarrow \quad \hat{J}_-|jm_{min}\rangle = 0 \quad \Longleftrightarrow \quad ||\hat{J}_-|jm_{min}\rangle||^2 = 0$$

$$\boxed{\Longleftrightarrow \qquad \lambda_j = \mu_{min}(\mu_{min} - \hbar)} \tag{4.70}$$

From eq. (4.69) and (4.70) it follows that

$$\boxed{\mu_{max} = -\mu_{min}} \tag{4.71}$$

We can move through the spectrum of $\hat{J}_z$ by applying ladder operators, e.g., we can start at μ_{max} and move towards the lower boundary μ_{min} by:

$$\begin{aligned} \hat{J}_z \hat{J}_-^n |jm_{max}\rangle &\overset{(4.64)}{=} (\hat{J}_-^n \hat{J}_z - n\hbar \hat{J}_-^n)|jm_{max}\rangle \\ &= (\mu_{max} - n\hbar)\hat{J}_-^n |jm_{max}\rangle \end{aligned}$$

$$\Longrightarrow \quad \exists \ n_0 \in \mathbb{N}_0 : \qquad \mu_{max} - n_0\hbar = \mu_{min} = -\mu_{max} \tag{4.72}$$

(i.e. we reach μ_{min} after n_0 steps; note that we cannot miss it due to eq. (4.70))

$\longrightarrow$ spectrum of $\hat{J}_z$ is quantized!

$$\begin{aligned} \overset{(4.72)}{\longrightarrow} \quad \mu_{max} &= \frac{n_0}{2}\hbar \equiv \hbar j = -\mu_{min} \\ &\text{with} \quad j = 0, \frac{1}{2}, 1, \frac{3}{2}, ... \end{aligned} \tag{4.73}$$

$$\begin{aligned} \hookrightarrow (4.70) \hookrightarrow \quad \lambda_j &= \hbar^2 j(j+1) \\ \text{and} \qquad \mu_m &= \hbar m \ , \qquad (m = -j, ..., j) \end{aligned} \tag{4.74}$$

Summary: angular momentum spectrum is discrete (quantized):

$$\begin{aligned} \hat{\mathbf{J}}^2 |jm\rangle &= \hbar^2 j(j+1)|jm\rangle \\ \hat{J}_z |jm\rangle &= \hbar m |jm\rangle \\ j &= 0, \frac{1}{2}, 1, \frac{3}{2}, ... \\ m &= \underbrace{-j, -j+1, ..., j-1, j}_{(2j+1) \text{ values } \rightarrow \text{ spectrum of } \mathbf{J}^2 \text{ is } (2j+1)-\text{fold degenerate}} \end{aligned} \tag{4.75}$$

$\hookrightarrow$ ladder operators

$$\hat{J}_+ |jm\rangle = \hbar\sqrt{j(j+1) - m(m+1)}|jm+1\rangle \tag{4.76}$$

$$\hat{J}_- |jm\rangle = \hbar\sqrt{j(j+1) - m(m-1)}|jm-1\rangle \tag{4.77}$$

4.3.2 Orbital angular momentum

(cf. chap. 3.3.5)

$$\hat{\mathbf{l}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$$

is an angular momentum operator

- One can show (see below) that eigenvalues are integer numbers:

$$\begin{aligned} \hat{\mathbf{l}}^2|lm\rangle &= \hbar^2 l(l+1)|lm\rangle \\ \hat{l}_z|lm\rangle &= m\hbar|lm\rangle \end{aligned}$$

l	=	0,	1,	2,	3,	...
spectroscopic notation		s	p	d	f,	...

- eigenvalue problem in coordinate space

$$\hat{l}_{z,(\mathbf{r})}\psi_{lm}(\mathbf{r}) \equiv \langle \mathbf{r}|\hat{l}_z|lm\rangle = i\hbar(y\partial_x - x\partial_y)\psi_{lm}(x,y,z)$$

- in spherical coordinates[1]

$$\hat{l}_{z,(\mathbf{r})}\psi_{lm}(\mathbf{r}) = \frac{\hbar}{i}\partial_\varphi \psi_{lm}(r,\theta,\varphi) \stackrel{!}{=} m\hbar\psi_{lm}(r,\theta,\varphi) \tag{4.78}$$

$$\hookrightarrow \quad \psi_{lm}(r,\theta,\varphi) = \chi_l(r,\theta)e^{im\varphi} \tag{4.79}$$

require that $\psi_{lm}(r,\theta,\varphi+2\pi) = \psi_{lm}(r,\theta,\varphi) \implies m$ integer!

correspondingly one finds after some calculation

$$\begin{aligned} \hat{\mathbf{l}}^2_{(\mathbf{r})}\psi_{lm}(r,\theta,\varphi) &= \Big\{ -\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) - \frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\Big\}\psi_{lm} \\ &\stackrel{!}{=} \hbar l(l+1)\psi_{lm} \end{aligned} \tag{4.80}$$

this partial differential equation is solved by the so-called

Spherical harmonics $Y_{lm}(\theta,\varphi)$

$$Y_{lm}(\theta,\varphi) = \sqrt{\frac{2l+1}{4\pi}\,\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\theta)e^{im\varphi} \tag{4.81}$$

$$P_l^m(x) = \frac{(-)^m}{2^l l!}(1-x^2)^{\frac{m}{2}}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l \tag{4.82}$$

[1]

$$\begin{aligned} x &= r\sin\theta\cos\varphi \\ y &= r\sin\theta\sin\varphi \\ z &= r\cos\theta \end{aligned}$$

'associated Legendre polynomials'

i.e. :	$\hat{\mathbf{l}}^2 Y_{lm}(\theta,\varphi) = \hbar^2 l(l+1) Y_{lm}(\theta,\varphi)$,	$l = 0, 1, 2, ...$
(cf. eq. (4.79), (4.80))	$\hat{l}_z Y_{lm}(\theta,\varphi) = m\hbar Y_{lm}(\theta,\varphi)$,	$m = -l, ..., l$

$\hookrightarrow$ Y_{lm} form a complete set of orthonormal functions (quadratically integrable) on unit sphere;

$$\text{i.e.} \qquad f(\theta,\varphi) = \sum_{lm} c_{lm} Y_{lm}(\theta,\varphi) \ , \quad \forall\ f(\theta,\varphi)$$

$$\text{and} \qquad \int Y^*_{l'm'}(\Omega) Y_{lm}(\Omega)\ d\Omega = \delta_{ll'}\delta_{mm'} \qquad (\text{with } \Omega = (\theta,\varphi))$$

$$\begin{aligned} Y_{00} &= \frac{1}{\sqrt{4\pi}} \\ Y_{10} &= \sqrt{\frac{3}{4\pi}}\cos\theta \\ Y_{11} &= -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\varphi} \\ Y_{1-1} &= \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi} \\ &(...) \end{aligned}$$

More details can be found, e.g., in: [Kirb], chap. 2.2.3; [Jac], chap. 3.5, 3.6; [Mes] QM I, Appendix B.4; [Lin]

(note that some authors use slightly different definitions of Y_{lm} or P_l^m)

4.3.3 Spin

What about half-integer angular momenta? Are they only acceptable mathematical solutions of the angular momentum eigenvalue problem or do they exist in nature? Let's consider the mathematics for the simplest case first and answer the question about its physical relevance afterwards!

a) Angular momentum algebra for $j \equiv s = \frac{1}{2}$

- eigenvalue equations (cf. eqs. (4.75)):

$$\hat{\mathbf{s}}^2 |s m_s\rangle \equiv \hat{\mathbf{s}}^2 |\frac{1}{2}, \pm\frac{1}{2}\rangle = \frac{3\hbar^2}{4} |\frac{1}{2}, \pm\frac{1}{2}\rangle \qquad (4.83)$$

$$\hat{s}_z |s m_s\rangle = \hat{s}_z |\frac{1}{2}, \pm\frac{1}{2}\rangle = \pm\frac{\hbar}{2} |\frac{1}{2}, \pm\frac{1}{2}\rangle \qquad (4.84)$$

$\longrightarrow$ two orthonormal spin functions exist:

$$\begin{aligned} |\frac{1}{2},+\frac{1}{2}\rangle &\equiv |\uparrow\rangle \qquad \text{"spin up"} \\ |\frac{1}{2},-\frac{1}{2}\rangle &\equiv |\downarrow\rangle \qquad \text{"spin down"} \end{aligned}$$

$\hookrightarrow \{|\uparrow\rangle, |\downarrow\rangle\}$ is orthonormal basis in this two-dimensional space

A general spin function $|\chi\rangle$ can be written as

$$|\chi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle \tag{4.85}$$

- Consider ladder operators (cf. eq. (4.76), (4.77))

$$\begin{aligned} \hat{s}_+|s,m_s\rangle &= \hbar\sqrt{s(s+1)-m_s(m_s+1)}\;|s,m_s+1\rangle \\ \hat{s}_-|s,m_s\rangle &= \hbar\sqrt{s(s+1)-m_s(m_s-1)}\;|s,m_s-1\rangle \end{aligned}$$

explicitly:

$$\hat{s}_+|\uparrow\rangle = \hat{s}_-|\downarrow\rangle = 0 \tag{4.86}$$

$$\hat{s}_+|\downarrow\rangle = \hbar|\uparrow\rangle \quad \searrow \tag{4.87}$$

$$\text{"spin}-\text{flips"}$$

$$\hat{s}_-|\uparrow\rangle = \hbar|\downarrow\rangle \quad \nearrow \tag{4.88}$$

- Matrix representation (2×2)

Vectors:

$$\begin{aligned} |\uparrow\rangle &\longrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ |\downarrow\rangle &\longrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ |\chi\rangle &\overset{(4.85)}{\longrightarrow} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \end{aligned}$$

Operators:

$$\begin{aligned} \hat{s}_z \longrightarrow \underline{\underline{s}}_z &= \begin{pmatrix} \langle\uparrow|\hat{s}_z|\uparrow\rangle & \langle\uparrow|\hat{s}_z|\downarrow\rangle \\ \langle\downarrow|\hat{s}_z|\uparrow\rangle & \langle\downarrow|\hat{s}_z|\downarrow\rangle \end{pmatrix} \\ &\overset{(4.83),(4.84)}{=} \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \tag{4.89}$$

correspondingly one finds from eqs. (4.83), (4.84) and (4.86) - (4.88): (and $\underline{\underline{s}}_x = \frac{1}{2}(\underline{\underline{s}}_+ + \underline{\underline{s}}_-)$, $\underline{\underline{s}}_y = \frac{1}{2i}(\underline{\underline{s}}_+ - \underline{\underline{s}}_-)$)

$$\underline{\underline{s}}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4.90}$$

$$\underline{\underline{s}}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{4.91}$$

$$\underline{\underline{s}}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{4.92}$$

Definition: Pauli's spin matrices

$$\underline{\underline{\sigma}}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \underline{\underline{\sigma}}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \underline{\underline{\sigma}}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

One can show that every 2×2 matrix can be represented as a linear combination of $\underline{\underline{\sigma}}_x$, $\underline{\underline{\sigma}}_y$, $\underline{\underline{\sigma}}_z$ and $\underline{\underline{1}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$.

b) Magnetic moments and spin hypothesis

Classical orbital angular momentum (of a charged particle) gives rise to a magnetic moment $\underline{\boldsymbol{\mu}}$.

$$\boldsymbol{\mu} \propto \mathbf{l} \tag{4.93}$$

Naive argument: consider charge q with circular motion:

$$\boldsymbol{\mu} = \underbrace{i\mathbf{F}}_{\text{"current} \times \text{ area"}} = \frac{qv}{2\pi r} \cdot \pi r^2 \mathbf{e}_\perp = \frac{qrv}{2}\mathbf{e}_\perp = \frac{q}{2m}\mathbf{l}$$

Better argument: [Kirb], chap. 3.3.3

$\hookrightarrow$ energy in external magnetic field

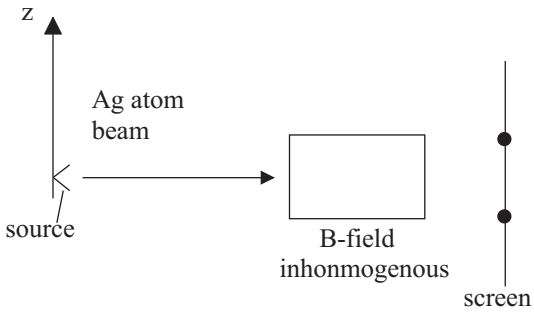
$$W = -\boldsymbol{\mu} \cdot \mathbf{B} \tag{4.94}$$

$$\hookrightarrow \text{ force } \quad \mathbf{F} = -\boldsymbol{\nabla} W = \begin{pmatrix} \mu_x \partial_x B_x \\ \mu_y \partial_y B_y \\ \mu_z \partial_z B_z \end{pmatrix} \tag{4.95}$$

$\longrightarrow$ deflection in inhomogeneous field!

$\hookrightarrow$ One can measure magnetic moment via deflection of (charged) particle in inhomogeneous B-field

$\longrightarrow$ Stern-Gerlach experiment (1922)



observation:
two distinct 'spots'
(where Ag atoms arrive)

Interpretation:

- quantize magnetic moment eq. (4.93) according to

$$\hat{\boldsymbol{\mu}} = \alpha \hat{\mathbf{l}} \ , \qquad (\alpha = \frac{q}{2m}) \tag{4.96}$$

- measure z-component of $\boldsymbol{\mu}$ $\longrightarrow$ i.e. eigenvalues of $\hat{\mu}_z$ (proportional to eigenvalues of $\hat{l}_z$)

$$\hookrightarrow \quad \mu_z = \alpha \hbar m \ , \qquad m = -l, ..., l \tag{4.97}$$

$\hookrightarrow$ the quantization of $\hat{l}_z$ explains why only distinct maxima are found instead of a continuous distribution. The number of spots must correspond to the number of possible eigenvalues of $\hat{\mu}_z$.

$\Longrightarrow$ Stern-Gerlach experiment can be understood if one assumes the existence of an intrinsic angular momentum $\hat{\mathbf{s}}$ (of an electron) with quantum numbers

$$s = \frac{1}{2} \ , \quad m_s = -\frac{1}{2}, \ \frac{1}{2} \ , \qquad \text{(spin doublet)}$$

(spin hypothesis by Goudsmit + Uhlenbeek, 1925)

This intrinsic angular momentum - the spin - is a new degree of freedom of a quantum particle without classical analogy. It is, however, connected with a magnetic moment (otherwise it would not be observable by Stern-Gerlach apparatus)

$$\hat{\boldsymbol{\mu}}_s = \beta \hat{\mathbf{s}} \tag{4.98}$$

One finds that constant β is different from $\alpha = -\frac{e}{2m}$ for the orbital angular motion (by a factor of 2; i.e. $\beta = -\frac{e}{m}$ for an electron). This

factor - as well as the Spin $\frac{1}{2}$ structure itself - can be derived without any ad hoc assumption or hand-waving arguments from the Dirac equation - the relativistic equation of motion for an electron (cf. chapter 5), which is why some authors consider spin a relativistic effect.

Note that Stern-Gerlach experiment was also performed with hydrogen atoms (i.e., one-electron systems) with the same result.

Further remarks:

- Spin hypothesis explains also the splitting of the spectral lines (of an atom) in an external (homogeneous) magnetic field ($\longrightarrow$ Zeeman effect)
- Not only electrons carry spin. In fact, quantum particles with integer and half-integer spin quantum numbers exist ($\longrightarrow$ spin-statistics theorem, chap. 3.5.5c).

c) Wave functions with spin

How to describe a quantum particle that carries spin and that has position (momentum) degrees of freedom?

Spin is independent of 'motion' of the particle, i.e.,

$$[f(\hat{x}_i, \hat{p}_i), g(\hat{s})] = 0$$

(for all operator functions)

$\longrightarrow$ state is a direct product state

$$|\Psi\rangle = \underbrace{|\psi\rangle}_{\text{orbital motion}} \quad \underbrace{|\chi\rangle}_{\text{spin}} \tag{4.99}$$

$$\begin{aligned} \Psi(\mathbf{r}) &= \langle \mathbf{r}|\Psi\rangle = \langle \mathbf{r}|\psi\rangle\Big(\alpha|\ \uparrow\rangle + \beta|\ \downarrow\rangle\Big) \\ &= \psi(\mathbf{r}) \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \equiv \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} \end{aligned} \tag{4.100}$$

$\longrightarrow$ two-component "spinor" wave function

Note that $\langle\Psi|\Psi\rangle = \langle\chi|\chi\rangle\langle\psi|\psi\rangle = 1 \times 1 = 1$

Consider a special decomposition:

$$\begin{aligned}\langle\Psi|\Psi\rangle &= \int \langle\Psi|\mathbf{r}\rangle\langle\mathbf{r}|\Psi\rangle \; d^3r \\ &= \int \Big(\psi_\uparrow^*(\mathbf{r}),\; \psi_\downarrow^*(\mathbf{r})\Big) \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} \; d^3r \\ &= \int \Big(|\psi_\uparrow(\mathbf{r})|^2 + |\psi_\downarrow(\mathbf{r})|^2\Big) \; d^3r \;\equiv\; \int \rho(\mathbf{r}) \; d^3r \\ &\qquad\qquad \uparrow \qquad\quad \uparrow \qquad\qquad \uparrow \\ &\qquad\qquad \text{spin}-\text{densities} \qquad \text{total density}\end{aligned}$$

Expectation values of spin operators $\hat{s}$:

$$\begin{aligned}\langle\hat{s}\rangle &= \langle\Psi|\hat{s}|\Psi\rangle \\ &= \int \Big(\psi_\uparrow^*(\mathbf{r}),\; \psi_\downarrow^*(\mathbf{r})\Big) \begin{pmatrix} s_{11} & s_{12} \\ s_{21} & s_{22} \end{pmatrix} \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} \; d^3r \\ &\equiv \int \langle S(\mathbf{r})\rangle \; d^3r\end{aligned}$$

$$\text{e.g.} \qquad \underline{\underline{s}}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hookrightarrow \quad \langle S_z(\mathbf{r})\rangle = \frac{\hbar}{2}\Big\{|\psi_\uparrow(\mathbf{r})|^2 - |\psi_\downarrow(\mathbf{r})|^2\Big\} \tag{4.101}$$

"net" spin at position $\mathbf{r}$ ('spin-excess')

d) Wave equation for particles with spin: Pauli equation

How to incorporate spin-dependent terms in Schrödinger equation?

- starting point: Hamiltonian for particle in EM field (eq. (2.52))

$$\hat{H} = \frac{1}{2m}\Big(\frac{\hbar}{i}\boldsymbol{\nabla} - q\mathbf{A}\Big)^2 + q\phi$$

- assume that particle (electron with q= -e) has spin $\frac{1}{2}$ $\hookrightarrow$ magnetic moment $\hat{\mu}_s$ (eq. (4.98) $\hookrightarrow$ energy W_s (eq. (4.94))
- add this energy

$$W_s = -\boldsymbol{\mu}_s \cdot \mathbf{B} = \mu_B \hat{\boldsymbol{\sigma}} \cdot \mathbf{B} \tag{4.102}$$

$\nwarrow$ Pauli matrices

$$\text{with} \qquad \mu_B = \frac{e\hbar}{2m} \qquad \text{'Bohr magneton'} \tag{4.103}$$

to Hamiltonian which then acts on spinor wave functions:

$$\hookrightarrow \quad i\hbar\partial_t\Psi = \hat{H}\Psi \tag{4.104}$$

$$\hat{H} = \frac{1}{2m}\Big(\frac{\hbar}{i}\nabla + e\mathbf{A}\Big)^2 - e\phi + \mu_B\hat{\boldsymbol{\sigma}}\cdot\mathbf{B} \tag{4.105}$$

$$\Psi = \begin{pmatrix} \psi_\uparrow(\mathbf{r}) \\ \psi_\downarrow(\mathbf{r}) \end{pmatrix} \qquad \longrightarrow \text{Pauli equation}$$

Remarks:

- Pauli equation describes Zeeman effect
- Spin-orbit coupling, i.e., the interaction of the spin of a bound electron with the magnetic field that originates from the relative motion of the nucleus can also be included in Pauli equation
- Pauli equation can be derived from Dirac equation (chapter 5) for $v \ll c$

4.3.4 Addition of angular momenta

Consider sum of angular momentum operators

$$\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \tag{4.106}$$

$\hookrightarrow$ $\hat{\mathbf{J}}$ is also angular momentum operator, i.e., has hermitian components which fulfill eqs. (4.56), (4.57).

Examples:

$\hat{\mathbf{j}} = \hat{\mathbf{l}} + \hat{\mathbf{s}}$	total angular momentum of a particle
$\hat{\mathbf{L}} = \sum_{i=1}^{N} \hat{\mathbf{l}}_i$	total orbital angular momentum of $N-$particle system
$\hat{\mathbf{S}} = \sum_{i=1}^{N} \hat{\mathbf{s}}_i$	total spin of $N-$particle system

$\longrightarrow$ all such angular momentum operators share the characteristic spectrum (eq. (4.75))

Question: How are quantum numbers and eigenvectors of $\hat{\mathbf{J}}^2,\ \hat{J}_z$ connected with those of $\hat{\mathbf{J}}_1^2,\ \hat{J}_{1z},\ \hat{\mathbf{J}}_2^2,\ \hat{J}_{2z}$?
$\hookrightarrow$ angular momentum coupling

Literature: [Mes], QM II, chap. 13.5; [Lin]; [CT], chap. 10

4.4 The hydrogen atom (and extensions)

Two-body problem for nucleus (n) and electron (e): (cf. chap. 2.2.4)

$$\hat{H} = \frac{\hat{\mathbf{p}}_n^2}{2m_n} + \frac{\hat{\mathbf{p}}_e^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0|\mathbf{r}_e - \mathbf{r}_n|} \tag{4.107}$$

$$m_n = 1836 m_e \; ; \quad m_e \approx 9.1 \times 10^{-31} \text{ kg}$$

4.4.1 Separation of the two-body problem

- Classical coordinate transformation (cf. [Kira], chap. 5.1.1)

$$(\mathbf{r}_e, \mathbf{p}_e, \mathbf{r}_n, \mathbf{p}_n) \quad \longrightarrow \quad (\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p})$$

definition :

$$\begin{aligned} M &= m_e + m_n \approx m_n \\ \mu &= \frac{m_e m_n}{m_e + m_n} \approx m_e \end{aligned}$$

$$\left.\begin{aligned} \mathbf{R} &= \tfrac{m_n\mathbf{r}_n + m_e\mathbf{r}_e}{M} \approx \mathbf{r}_n \\ \mathbf{P} &= \mathbf{p}_e + \mathbf{p}_n = M\dot{\mathbf{R}} \approx \mathbf{p}_n \end{aligned}\right\} \text{center-of-mass motion}$$

$$\left.\begin{aligned} \mathbf{r} &= \mathbf{r}_e - \mathbf{r}_n \\ \mathbf{p} &= \mu\dot{\mathbf{r}} = \tfrac{m_n\mathbf{p}_e - m_e\mathbf{p}_n}{M} \end{aligned}\right\} \text{relative motion}$$

- QM transformation analogously

$$(\hat{\mathbf{r}}_e, \hat{\mathbf{p}}_e, \hat{\mathbf{r}}_n, \hat{\mathbf{p}}_n) \quad \longrightarrow \quad (\hat{\mathbf{R}}, \hat{\mathbf{P}}, \hat{\mathbf{r}}, \hat{\mathbf{p}}) \tag{4.108}$$

insertion in eq. (4.107) yields

$$\begin{aligned} \hat{H} &= \frac{\hat{\mathbf{P}}^2}{2M} + \frac{\hat{\mathbf{p}}^2}{2\mu} + V(\hat{r}) \; , \qquad \left(V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}\right) \\ &= \hat{H}_{CM} + \hat{H}_{rel} \end{aligned} \tag{4.109}$$

eq. (4.109) is the Hamiltonian of a non-interacting two-(quasi-)particle system $\hookrightarrow$ can be separated into one-particle problems (cf. chap. 3.5.5c):

Ansatz :

$$|\Psi\rangle = |\Phi_{CM}\varphi_{rel}\rangle \tag{4.110}$$

(i.e. $\Psi(\mathbf{r}, \mathbf{R}) = \Phi_{CM}(\mathbf{R})\varphi_{rel}(\mathbf{r})$ in coordinate space)

$\hookrightarrow$ Schrödinger eqs.

$$\hat{H}_{CM}|\Phi_{CM}\rangle = E_{CM}|\Phi_{CM}\rangle \quad (4.111)$$

$$\hat{H}_{rel}|\varphi_{rel}\rangle = E_{rel}|\varphi_{rel}\rangle \quad (4.112)$$

and

$$\hat{H}|\Psi\rangle = (E_{CM} + E_{rel})|\Psi\rangle \quad (4.113)$$

SE (4.111) can be solved without difficulty:

$$\hookrightarrow \quad \left.\begin{aligned} \Phi_{CM}(\mathbf{R}) &= Ae^{i\mathbf{KR}} \\ \mathbf{K} &= \tfrac{1}{\hbar}\mathbf{P} \\ E_{CM} &= \tfrac{\hbar^2\mathbf{K}^2}{2M} \end{aligned}\right\} \text{free} - \text{particle motion}$$

eq. (4.112) can also be solved analytically, but before we sketch the solution we consider some general properties/features of the quantum central-field ($V(\mathbf{r}) = V(r)$) problem.

4.4.2 The QM central-field problem

Consider

$$\hat{H}_{rel} = \frac{\hat{\mathbf{p}}^2}{2\mu} + V(r) \quad (4.114)$$

One can show that $\hat{H}_{rel}$ is invariant with respect to any rotation $\hat{R}$ (cf. chap. 3.5.4a), i.e.

$$[\hat{H}_{rel}, \hat{R}] = 0$$

$$\Longrightarrow \quad [\hat{H}_{rel}, \hat{\mathbf{l}}] = 0 \quad (4.115)$$

$\nwarrow$ conservation of angular momentum!

In particular, the operators $\hat{H}_{rel}, \hat{\mathbf{l}}^2, \hat{l}_z$ form a complete set of compatible operators (cf. page 72), i.e.,

$$[\hat{H}_{rel}, \hat{\mathbf{l}}^2] = [\hat{H}_{rel}, \hat{l}_z] = [\hat{\mathbf{l}}^2, \hat{l}_z] = 0 \quad (4.116)$$

$\hookrightarrow$ they have a common set of eigenstates. The eigenstates of $\hat{\mathbf{l}}^2, \hat{l}_z$ are the spherical harmonics Y_{lm} (4.81);

$$\hookrightarrow \quad \text{ansatz} \qquad \varphi_{rel}(\mathbf{r}) = R_l(r)Y_{lm}(\theta, \varphi) \quad (4.117)$$

Insertion into (4.112) for Hamiltonian (4.114) yields radial SE:

$$\left\{\frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) - E\right\} R_l(r) = 0 \quad (4.118)$$

$$\text{with} \qquad \hat{p}_r^2 = -\frac{\hbar^2}{r^2}\partial_r(r^2\partial_r)$$

$$\text{and operator identity} \qquad \hat{\mathbf{p}}^2 = \hat{p}_r^2 + \frac{\hat{\mathbf{l}}^2}{r^2}$$

(can be proven in spherical coordinates in coordinate space)

$$\text{useful definition :} \qquad y_l(r) = rR_l(r) \tag{4.119}$$

$$\overset{(4.118)}{\hookrightarrow} \qquad y_l''(r) + \Big[\epsilon - U(r) - \frac{l(l+1)}{r^2}\Big] y_l(r) = 0 \tag{4.120}$$

$$\Big(E = \frac{\hbar^2}{2\mu}\epsilon\ , \quad V(r) = \frac{\hbar^2}{2\mu}U(r)\Big)$$

The radial eq. (4.120) is very similar to the 1D-SE (2.86). There are, however, two important differences:

(i) 'Effective' potential in eq. (4.120)

$$U_l^{eff}(r) = U(r) + \frac{l(l+1)}{r^2}$$

$\nwarrow$ "angular momentum barrier"

(cf. classical central-field problem)

(ii) boundary conditions

- $|\varphi_{rel}(\mathbf{r})|^2 = |R_l(r)|^2 |Y_{lm}(\theta,\varphi)|^2 < \infty$
  in particular for $\mathbf{r} = 0$
  $\hookrightarrow$ 'regularity condition'

$$y_l(0) = 0 \tag{4.121}$$

- $r \longrightarrow \infty$

  (a) $E < 0$ (bound spectrum)

$$\int |\varphi_{rel}(\mathbf{r})|^2\ d^3r = \int_0^\infty r^2 R_l^2(r)\ dr \int |Y_{lm}(\theta,\varphi)|^2\ d\Omega$$
$$= \int_0^\infty y_l^2(r)\ dr\ <\ \infty$$

  (quadratically integrable solutions required)

$$\hookrightarrow \quad y_l(r) \overset{r\to\infty}{\longrightarrow} 0 \qquad \text{(boundary condition)}$$

  (b) $E > 0$ (continuous spectrum)
  $\hookrightarrow$ oscillatory solutions $y_l(r)$ for $r \longrightarrow \infty$

4.4.3 Solution of the Coulomb problem ($E < 0$)

(note: for $E > 0$ the solution leads to Rutherford's scattering formula (which is identical in classical mechanics and QM))

$$\begin{aligned} \text{definition :} \qquad \kappa^2 &= -\epsilon > 0 \\ a &= \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} \approx 0.53 \cdot 10^{-10}\ \text{m} \\ \text{for} \qquad \mu &\equiv m_e\ , \quad a \equiv a_0 \qquad \text{is the 'Bohr radius'} \end{aligned}$$

$\hookrightarrow$ radial eq. (4.120):

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + \frac{2Z}{ar} - \kappa^2\right) y_l(r) = 0 \tag{4.122}$$

transformation: $x = 2\kappa r$

$$\hookrightarrow \quad \frac{d^2}{dx^2} = \frac{1}{4\kappa^2}\frac{d^2}{dr^2}$$

$$\hookrightarrow \quad \left(\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2} + \frac{\lambda}{x} - \frac{1}{4}\right) y_l(x) = 0 \tag{4.123}$$

asymptotic solutions:

1. $x \longrightarrow \infty$

$$\hookrightarrow \quad \left(\frac{d^2}{dx^2} - \frac{1}{4}\right) y_l(x) = 0$$

$$\hookrightarrow \quad y_l(x) = Ae^{-\frac{x}{2}} + Be^{\frac{x}{2}}$$

because of $y_l(x \to \infty) = 0 \quad \hookrightarrow \ B = 0$

2. $x \longrightarrow 0$

$$\hookrightarrow \quad \left(\frac{d^2}{dx^2} - \frac{l(l+1)}{x^2}\right) y_l(x) = 0$$

$$\hookrightarrow \quad y_l(x) = \frac{A}{x^l} + Bx^{l+1}$$

because of $y_l(0) = 0 \quad \hookrightarrow \ A = 0$

This consideration motivates the following ansatz:

$$y_l(x) = x^{l+1}e^{-\frac{x}{2}}v_l(x) \tag{4.124}$$

Insertion into eq. (4.123) yields new differential eq. for $v_l(x)$:

$$\hookrightarrow \quad \left\{ x\frac{d^2}{dx^2} + (2l+2-x)\frac{d}{dx} - (l+1-\lambda) \right\} v_l(x) = 0 \tag{4.125}$$

The quadratically integrable solution of (4.125) ('Kummer's' or 'Laplace's' differential eq.) are known; they are the associated Laguerre polynomials:

$$L_p^k(x) = \sum_{j=0}^{p} (-)^j \frac{\left[(p+k)!\right]^2}{(p-j)!(k+j)!j!} x^j$$

more specifically:

$$v_l(x) = L_{n-l-1}^{2l+1}(x) \ , \qquad \left(\begin{array}{c} n_r = n-l-1 \geq 0 \\ \Longleftrightarrow \quad n-1 \geq l \end{array} \right)$$

$$\text{with} \qquad n \equiv \lambda_n = \frac{Z}{\kappa_n a} \ , \qquad n = 1, 2, ... \tag{4.126}$$

The detailed solution shows that the integrability of the solutions requires $\lambda = \frac{Z}{\kappa a}$ to be positive, integer numbers $\longrightarrow$ quantization of κ (i.e. quantization of the energy)[2]

$$\hookrightarrow \quad y_{nl}(\mathbf{r}) = A_{nl} r^{l+1} e^{-\kappa_n r} L_{n-l-1}^{2l+1}(2\kappa_n r)$$

and properly normalized wave functions take the form

$$\begin{aligned} \varphi_{rel}(\mathbf{r}) \equiv \varphi_{nlm}(\mathbf{r}) &= \frac{(n-l-1)!}{\left[(n+l)!\right]^3} 2^{l+\frac{1}{2}} \kappa_n^{l+2} \sqrt{a} \\ &\quad \times r^l e^{-\kappa_n r} L_{n-l-1}^{2l+1}(2\kappa_n r) Y_{lm}(\theta, \varphi) \\ &\equiv R_{nl}(r) Y_{lm}(\theta, \varphi) \ , \qquad \begin{array}{l} n \geq 0 \\ l \leq n-1 \\ -l \leq m \leq l \end{array} \end{aligned} \tag{4.127}$$

quantization condition (4.126) leads to:

$$E_n = -\frac{RZ^2}{n^2} \ , \qquad n = 1, 2, ... \tag{4.128}$$

$$R = \frac{\hbar^2}{2\mu a^2} \approx 13.6 \text{ V} \qquad \text{"Rydberg" constant} \tag{4.129}$$

[2] One can find the quadratically integrable solutions of (4.125) explicitly by using the ansatz $v_l(x) = \sum_i b_i^l x^i$ and by taking the boundary (and regularity) conditions into account.

The lowest-lying hydrogen eigenfunctions ('orbitals')

n	l	m	$n_r = n-l-1$		$\varphi_{nlm}(\mathbf{r})$	$-E_n$
1	0	0	0	1s	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a}}$	RZ^2
2	0	0	1	2s	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a}\right)e^{-\frac{Zr}{2a}}$	$\frac{RZ^2}{4}$
2	1	0	0	$2p_0$	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(\frac{Zr}{a}\right)e^{-\frac{Zr}{2a}}\cos\theta$	$\frac{RZ^2}{4}$
2	1	± 1	0	$2p_{\pm 1}$	$\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a}\right)^{\frac{3}{2}}\left(\frac{Zr}{a}\right)e^{-\frac{Zr}{2a}}\sin\theta e^{\pm i\varphi}$	$\frac{RZ^2}{4}$

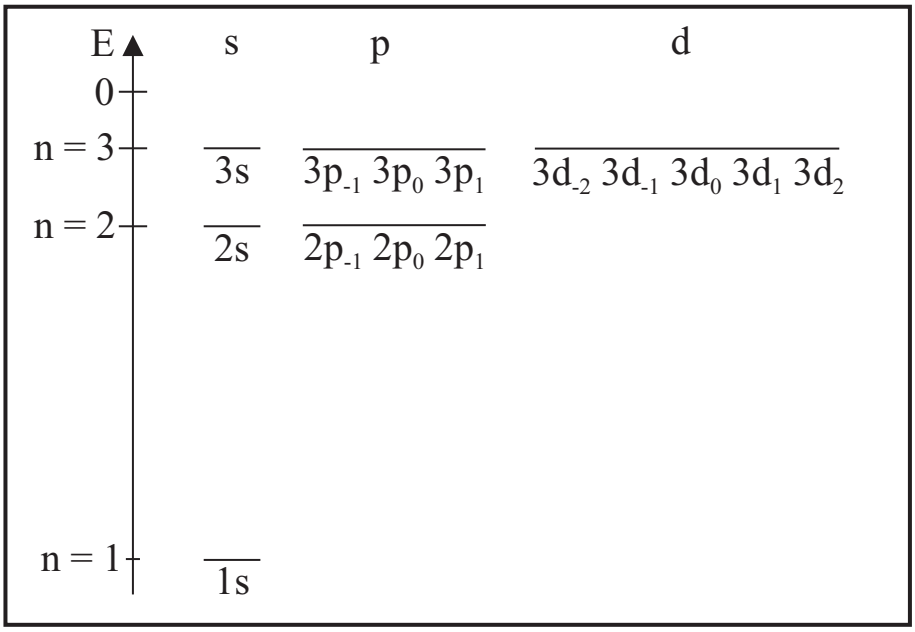


Figure 4.2: Energy spectrum of the Schrödinger-Coulomb problem. Note that Coulomb potential supports infinitely many bound states ($E_n \overset{n\to\infty}{\longrightarrow} 0$).

Degeneracy of energies (depend only on n)

given n $\quad l = 0, 1, ..., n-1$
given l $\quad m = -l, ..., l$

$$\hookrightarrow \quad \sum_{l=0}^{n-1}(2l+1) = n^2$$

$\longrightarrow$ each energy level E_n is n^2-fold degenerate. Note that all central-field problems share $(2l+1)$-fold degeneracy originating from rotational invariance. The fact that energies do not depend on n_r, l separately, but only on $n = n_r + l + 1$

is specific to the Coulomb problem (one denotes n as the 'principal' quantum number, and n_r as the 'radial' quantum number which determines the number of nodes in the radial wave functions).

Often one considers a radial probability density defined by

$$\begin{aligned} \rho_{nl}(r) &= r^2 R_{nl}^2(r) \int |Y_{lm}(\theta,\varphi)|^2 \, d\Omega \\ &= y_{nl}^2(r) \end{aligned} \tag{4.130}$$

$\rho_{nl}(r)\, dr$: probability to find electron at radial distance $[r, r+dr]$

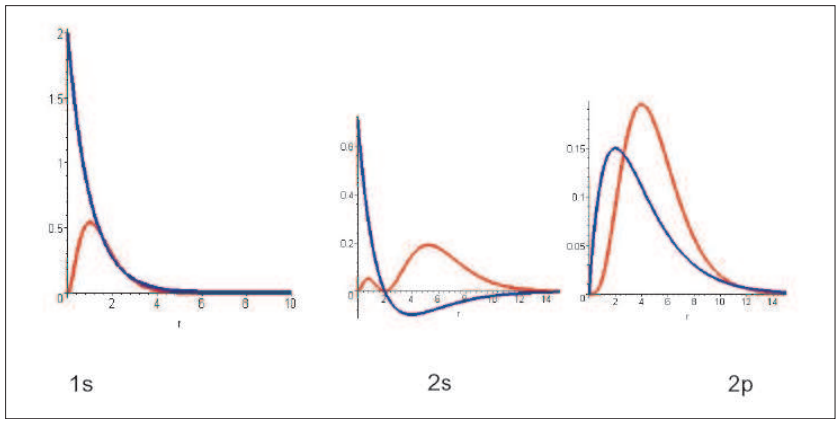


Figure 4.3: Radial hydrogen 1s, 2s, 2p wave functions (blue) and probability densities (red)

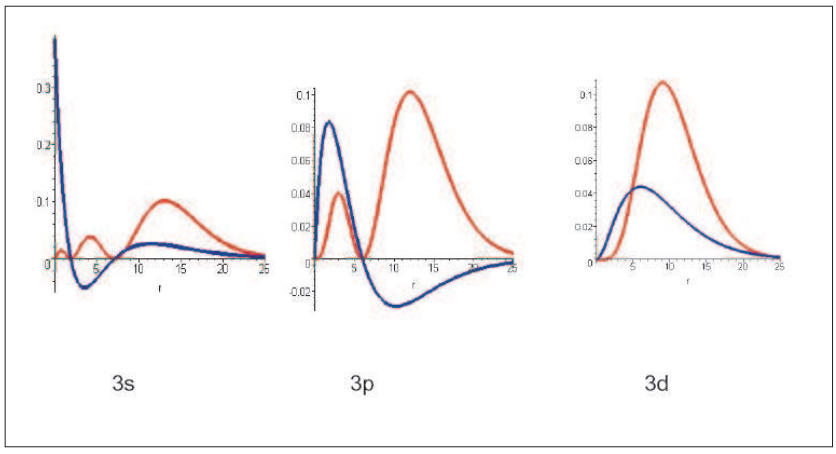


Figure 4.4: Radial hydrogen 3s, 3p, 3d wave functions (blue) and probability densities (red)

4.4.4 Assorted remarks

a) More (mathematical) details about the Coulomb problem can be found in any QM textbook!

b) Hydrogen-like ions

We have solved not only the (Schrödinger) hydrogen problem ($Z = 1$), but also the bound-state problems of all one-electron atomic ions (e.g. He^+, Li^{2+},...) for $Z = 2, 3, ...$

c) Exotic systems

... are also solved

(a) positronium (e^+e^-)

(b) myonium (μ^+e^-)

(c) myonic atom ($p\mu^-$)

In these cases one has to take care of the different masses compared to the hydrogen problem (p^+e^-); ($m_\mu \approx 207\ m_e$)

d) Corrections

The spectrum determined by eq. (4.128) is the exact solution of the Schrödinger-Coulomb problem, but not exactly what one sees experimentally. The reason is that the Schrödinger equation is not the ultimate answer, e.g., it has to be modified to meet the requirements of the theory of special relativity. Therefore, corrections show up (cf. chapter 5), which lead to a (partial) lifting of the degeneracy.

e) Many-electron atoms

... cannot be solved analytically!

One approach to approximate solutions: stationary perturbation theory.

Let's consider the He atom (2 electrons) with 'fixed' nucleus (i.e. $m_n \to \infty$).

$$\begin{aligned} \hat{H} &= -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0|\mathbf{r}_1 - \mathbf{r}_r|} \\ &= \qquad\qquad \hat{H}_0 \qquad\qquad\qquad + \quad \hat{V}_{12} \end{aligned} \tag{4.131}$$

- 0^{th} order approximation: $\hat{V}_{12} = 0$
  $\hookrightarrow$ $\hat{H}_0$ is the non-interacting Hamiltonian.
  Note that we have to take care about the Pauli principle because we deal with a many-particle fermionic system.

The antisymmetric ground-state wave function reads:

$$\Psi_0^- = \varphi_{1s}^{He^+}(r_1)\varphi_{1s}^{He^+}(r_2) \cdot \underbrace{\frac{1}{\sqrt{2}}\Big(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\Big)}_{\text{"spin singlet"}} \qquad (4.132)$$

I.e., we have filled the "K"-shell ($n = 1$) with 2 electrons with opposite spin such that Ψ_0^- be antisymmetric.

Since the Hamiltonian (4.131) does not include spin-dependent interactions only the spatial part of Ψ_0 is needed to determine the ground-state energy (from eq. (4.128)):

$$\begin{aligned} E_0^{(0)} &= -8R &&= -108.8 \text{ eV} \\ E_0^{expt} &= &&= -79 \text{ eV} \end{aligned}$$

This is obviously a poor approximation

- 1^{st} order approximation

  We can improve the calculation by consideration of the first-order correction according to eq. (4.28):

$$\begin{aligned} E_0^{(1)} &= \langle\Psi_0|\hat{V}_{12}|\Psi_0\rangle \\ &= \frac{e^2}{4\pi\epsilon_0}\int d^3r_1 \int d^3r_2 \Big(\frac{1}{\pi^2}\Big(\frac{Z}{a_0}^6\Big)\Big)\frac{e^{-\frac{2Zr_1}{a_0}}e^{-\frac{2Zr_2}{a_0}}}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ &= \quad \ldots \quad = \frac{5}{8}\frac{Ze^2}{a_0} \end{aligned}$$

  for $Z = 2$ we obtain $E^{(1)} = 34$ eV, and

$$E_0^{(1)} = E_0^{(0)} + E^{(1)} = -74.8 \text{ eV}$$

  which is a considerable improvement!

- Better starting point for 1^{st} order perturbation theory

$$\begin{aligned} \hat{H} &= \Big[\hat{H}_0 + v_{eff}(r_1) + v_{eff}(r_2)\Big] + \Big[\hat{V}_{12} - v_{eff}(r_1) - v_{eff}(r_2)\Big] \\ &= \qquad \hat{H}_0' \qquad + \qquad \hat{V}_{12}' \end{aligned}$$

  idea: subtract a 'mean-field potential' v_{eff} from the electron-electron repulsion $\hat{V}_{12}$, solve modified $\hat{H}_0'$-problem, and calculate $\langle\Psi_0'|\hat{V}_{12}'|\Psi_0'\rangle$ as the 1^{st} order correction. As some parts of the electron-electron interaction are now included in $\hat{H}_0'$, $\hat{V}_{12}'$ should be a smaller perturbation than $\hat{V}_{12}$, and the 1^{st} order result should be more accurate.

The systematic consideration of this idea leads to the so-called 'independent particle model' (IPM), and, in particular, to the Hartree-Fock method (one has to find reasonable mean-field potentials v_{eff}, and in Hartree-Fock theory on uses the variational principle to find the 'best' one).

Within the IPM the main characteristics of the (shell-structure of) atoms (and the periodic table) can be understood.

- Another road that can be taken to find better approximations for E_0 for a many-electron atom is to use the variational principle to construct approximate two-electron wave functions (beyond IPM models). This has been very successful for small atoms, but is computationally costly for true many-electron atoms/systems.
  (the most accurate solutions to date - e.g. for He - are obtained along these lines)

f) Bound atoms $\longrightarrow$ molecules

The simplest idea of a molecule is one with fixed nuclei. Then, we have to solve the SE for the electrons in a multiple-center Coulomb potential. The more complicated geometry makes this more challenging, but such calculations can be done, e.g., on the level of the IPM (Hartree Fock), and many aspects of the structure of molecules (e.g., the existence of stable bonds) can be understood in this fashion. More quantitative/complete calculations require refinements, i.e., electronic structure calculations beyond the IPM, and an account of the nuclear motion.

A (qualitive) discussion of molecules and chemical bonds can be found in [Blöc], chap. 14.

Chapter 5

Brief introduction into relativistic Quantum Mechanics

Literature: [BD]; [BS]; [Schb], II; [Jel], II and [Scha], chap. 13. The latter two sources provide condensed accounts on relativistic Quantum Mechanics.

5.1 Klein-Gordon equation

5.1.1 Formulation

- Relativistic energy-momentum relation (classical)

$$E^2 = \mathbf{p}^2 c^2 + m_0^2 c^4 \tag{5.1}$$

- 'Quantization' : (correspondence rules)

$$\begin{aligned} E &\longrightarrow i\hbar\partial_t \\ \mathbf{p} &\longrightarrow \frac{\hbar}{i}\boldsymbol{\nabla} \\ \hookrightarrow \quad E^2 &\longrightarrow -\hbar^2\partial_t \end{aligned}$$

- (free) wave equation (Klein-Gordon equation (KGE))

$$-\hbar^2\partial_{t^2}\psi(\mathbf{r},t) = -\hbar^2 c^2\Delta\psi(\mathbf{r},t) + m_0^2 c^4\psi(\mathbf{r},t) \tag{5.2}$$

  first 'derived' by Schrödinger in winter 1925/26

5.1.2 Discussion

1. KGE is invariant under Lorentz transformations
2. Time development is determined via initial conditions $\psi(t_0)$, $\frac{\partial\psi}{\partial t}(t_0)$ since KGE is (partial) differential eq. of second order in t (and in $\mathbf{r}$).

3. Continuity equation?

   $\longrightarrow$ one can derive $\partial_t \rho + div\mathbf{j} = 0$ (cf. eq. (2.62)

   with $\mathbf{j} = \frac{i\hbar}{2m}(\psi \boldsymbol{\nabla}\psi^* - \psi^* \boldsymbol{\nabla}\psi)$ (as usual; cf. eq. (2.62))

   $$\text{but :} \qquad \rho = \frac{i\hbar}{2mc^2}(\psi^* \partial_t \psi - \psi \partial_t \psi^*) \tag{5.3}$$

   problem: $\rho(\mathbf{r}t) \gtrless 0$ (i.e. not positive definite)
   $\longrightarrow$ probabilistic interpretation is not possible (or at least not obvious)

4. Ansatz:

   $$\psi(\mathbf{r}, t) = Ae^{i(\mathbf{kr}-\omega t)}$$

   $\longrightarrow$ insertion in eq. (5.2) yields together with de Broglie relations

   $$E = \hbar\omega = \pm\sqrt{c^2\mathbf{p}^2 + m_0^2 c^4} \lessgtr 0 \tag{5.4}$$

   Meaning of $E < 0$ solution?

5. Add Coulomb potential to free KGE and solve it (in spherical coordinates) $\longrightarrow$ yields wrong 'fine structure' of hydrogen spectrum (i.e. contradicts experimental findings)

6. In 1934 KGE was recognized as correct wave equation for spin-0 particles (mesons).

5.2 Dirac equation

In 1928, Dirac found a new wave equation which is suitable for electrons (spin $\frac{1}{2}$-particles): the Dirac equation (DE)

5.2.1 Construction of the free DE

$$\text{Ansatz :} \qquad i\hbar\partial_t \Psi = \hat{H}_D \Psi \tag{5.5}$$

i.e. stick to the form of the TDSE; a partial differential eq. of 1^{st} order in t such that $\Psi(t_0)$ is the only initial condition (see postulate 3.3.6)

Requirements:

1. DE must be compatible with energy-momentum relation (5.1)
2. DE must be Lorentz-covariant
3. Continuity equation with probabilistic interpretation

4. Stick to quantization rules!

Dirac recognized that these requirements cannot be satisfied by a single scalar equation, but by a matrix equation for a spinor wave function with N components.

$$\text{Ansatz}: \quad \hat{H}_D = c\boldsymbol{\alpha}\hat{\mathbf{p}} + \beta m_0 c^2 = \frac{c\hbar}{i}\sum_{j=1}^{3}\alpha_i \partial_{x_i} + \beta m_0 c^2 \tag{5.6}$$

with $N \times N$ matrices $\alpha_x, \alpha_y, \alpha_z, \beta$ and spinor wave function

$$\Psi = \begin{pmatrix} \psi_1(\mathbf{r},t) \\ \vdots \\ \psi_N(\mathbf{r},t) \end{pmatrix} \qquad \text{as solution of (5.5)}$$

$\hookrightarrow$ requirement (1) is met if each component ψ_i solves KGE (5.2)
$\longrightarrow$ iterate eq. (5.5):

$$i\hbar\partial_t(i\hbar\partial_t\Psi) = \hat{H}_D(\hat{H}_D\Psi)$$

$$\begin{aligned}
\hookrightarrow \quad -\hbar^2\partial_{t^2}\Psi &= \Big(\frac{c\hbar}{i}\sum_j \alpha_j\partial_{x_j} + \beta m_0c^2\Big)\Big(\frac{c\hbar}{i}\sum_k \alpha_k\partial_{x_k} + \beta m_0c^2\Big)\Psi \\
&= \Big\{-\hbar^2c^2\sum_{jk}\alpha_j\alpha_k\partial_{x_j}\partial_{x_k} + \frac{\hbar}{i}m_0c^3\sum_j\big(\alpha_j\beta+\beta\alpha_j\big)\partial_{x_j} + \beta^2m_0^2c^4\Big\}\Psi \\
&= -\hbar^2c^2\sum_{jk}\frac{\alpha_j\alpha_k+\alpha_k\alpha_j}{2}\partial^2_{x_jx_k}\Psi + \beta^2m_0^2c^4\Psi + \frac{\hbar mc^3}{i}\sum_j(\alpha_j\beta+\beta\alpha_j)\partial_{x_j}\Psi
\end{aligned}$$

comparison with KGE yields conditions for α_i, β:

$$\alpha_j\alpha_k + \alpha_k\alpha_j = 2\delta_{jk} \tag{5.7}$$
$$\alpha_j\beta + \beta\alpha_j = 0 \tag{5.8}$$
$$\alpha_j^2 = \beta^2 = 1 \tag{5.9}$$

Further conditions and consequences:

- α_j, β hermitian (because $\hat{H}_D$ shall be hermitian)
  $\Longrightarrow$ real eigenvalues
  $\overset{5.9}{\Longrightarrow}$ eigenvalues are ± 1

- From (5.7)-(5.9) it follows that α_j, β are 'traceless', i.e.
  $tr\ \alpha_j = tr\ \beta = 0$[1]

[1]The trace of a matrix $\underline{\underline{A}}$ is defined as the sum over the diagonal elements. The trace does not change when $\underline{\underline{A}}$ is diagonalized. Hence $tr\ \underline{\underline{A}} = \sum$ eigenvalues.

- Together with eigenvalues ± 1 this implies that dimension N is <u>even</u>
- $N = 2$ is too small as there are only three (but not 4) 'anti-commuting' (eqs. (5.7) and (5.8)) matrices for $N = 2$ (the Pauli matrices)
- try $N = 4$
- derive explicit representations from these conditions

$$\hookrightarrow \quad \alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix} , \qquad \beta = \begin{pmatrix} 1 & & & 0 \\ & 1 & & \\ & & -1 & \\ 0 & & & -1 \end{pmatrix} \tag{5.10}$$

  with Pauli matrices σ_i

$\Longrightarrow$ free DE takes the form

$$i\hbar\partial_t \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} = (c\boldsymbol{\alpha} \cdot \hat{\mathbf{p}} + \beta m_0 c^2) \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \tag{5.11}$$

and one can derive a meaningful continuity equation:

$$\partial_t \rho + div\mathbf{j} = 0$$

with $$\rho = \Psi^\dagger\Psi = \sum_{i=1}^{4} \psi^*(\mathbf{r},t)\psi(\mathbf{r},t)$$

and $$\mathbf{j} = c\Psi^\dagger\boldsymbol{\alpha}\Psi$$

$$\left(\text{ i.e. } \quad j_k = c(\psi_1^*, \psi_2^*, \psi_3^*, \psi_4^*) \begin{pmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \psi_4 \end{pmatrix} \right)$$

5.2.2 Solutions of the free DE

Ansatz : $$\psi_j(\mathbf{r},t) = u_j e^{i(\mathbf{kr}-\omega t)} , \qquad j = 1, ..., 4$$

after some calculation one finds:

- there are 4 linear independent solutions.

Two correspond to $$E = +\sqrt{\mathbf{p}^2c^2 + m_0^2c^4}$$

and two to $$E = -\sqrt{\mathbf{p}^2c^2 + m_0^2c^4}$$

- they have the form ($E > 0$):

$$u^{(1)} = \begin{pmatrix} 1 \\ 0 \\ \chi_1 \\ \chi_2 \end{pmatrix} , \qquad u^{(2)} = \begin{pmatrix} 0 \\ 1 \\ \chi_1' \\ \chi_2' \end{pmatrix}$$

(and similarly for $E < 0$)
with $\chi_1, \chi_2, \chi_1', \chi_2' \overset{v \ll c}{\longrightarrow} 0$: 'small components'

$u^{(1)}$ is interpreted as 'spin up'
$u^{(2)}$ is interpreted as 'spin down' solution

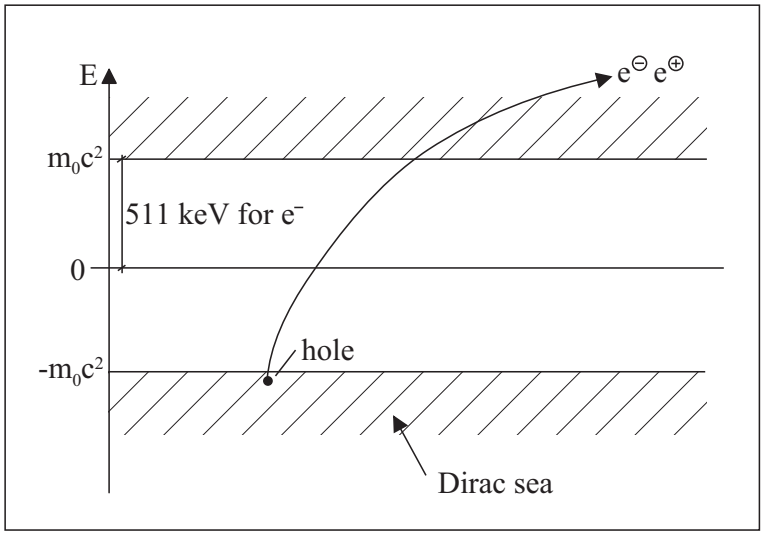


Figure 5.1: Energy spectrum

Dirac's interpretation: ('hole theory')

In the vacuum all negative energy states (in the Dirac sea) are occupied. Hence, if electrons are present at $E > m_0c^2$ they cannot "fall down" into the Dirac sea because of the Pauli principle.

On the other hand, one can imagine that it is possible to excite one electron from the Dirac sea to $E > m_0c^2$. Such an excitation corresponds to a hole in the Dirac sea, which can be interpreted as the presence of a positively charged particle - an anti-particle (i.e. a positron). This process - electron-positron pair creation - has indeed been observed, and also the reversed process - destruction of electron-positron pairs and γ-ray emission (the latter to balance the total energy).

In fact, the first experimental detection of positrons in 1932 was considered a strong proof of Dirac's theory.

5.2.3 Electromagnetic potentials

'minimal coupling prescription' (cf. chap. 2.2.3)

$$\begin{aligned} \mathbf{p} &\longrightarrow \frac{\hbar}{i}\boldsymbol{\nabla} - q\mathbf{A} \;=\; \hat{\mathbf{p}} - q\mathbf{A} \\ E &\longrightarrow i\hbar\partial_t - q\phi \end{aligned}$$

$$\overset{5.11}{\hookrightarrow} \quad i\hbar\partial_t\Psi = \Big\{c\hat{\boldsymbol{\alpha}}(\hat{\mathbf{p}} - q\mathbf{A}) + q\phi + \beta m_0 c^2\Big\}\Psi \tag{5.12}$$

indeed, one can show that eq. (5.12) is Lorentz-covariant

5.2.4 Relativistic hydrogen atom

Consider eq. (5.12) with $\mathbf{A} = 0$ and

$$q\phi = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

Ansatz : $$\Psi(\mathbf{r},t) = \Psi(\mathbf{r})e^{-\frac{i}{\hbar}Et} \tag{5.13}$$

(cf. eq. (2.84))

$$\overset{\text{yields}}{\longrightarrow} \qquad \Big\{c\hat{\boldsymbol{\alpha}}\hat{\mathbf{p}} + \beta m_0 c^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\Big\}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{5.14}$$

can be solved analytically!

Result for bound spectrum ($\longrightarrow$ fine structure)
$\longrightarrow$ quantized energy levels:

$$E_{nj} \;=\; m_0c^2\left[1 + \frac{(Z\alpha)^2}{(n-\delta_j)^2}\right]^{-\frac{1}{2}} \tag{5.15}$$

$$\delta_j \;=\; j + \frac{1}{2} - \sqrt{\Big(j+\frac{1}{2}\Big)^2 - (Z\alpha)^2}\,, \qquad j = \frac{1}{2}, \frac{3}{2}, ... \tag{5.16}$$

(j can be identified as quantum number of total angular momentum)

$$\alpha = \frac{\hbar}{mca_0} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \tag{5.17}$$

'fine-structure constant'

Expansion cf. eq. (5.15) in powers of $Z\alpha \ll 1$:

$$E_{nj} = m_0c^2\left[1 - \frac{(Z\alpha)^2}{2n^2} - \frac{(Z\alpha)^4}{2n^3}\Big(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\Big) \pm ...\right] \tag{5.18}$$

1^{st} term: rest energy
2^{nd} term: non-relativistic binding energy (4.128)
3^{rd} term: lowest order relativistic corrections $\longrightarrow$ fine structure splitting of energy levels

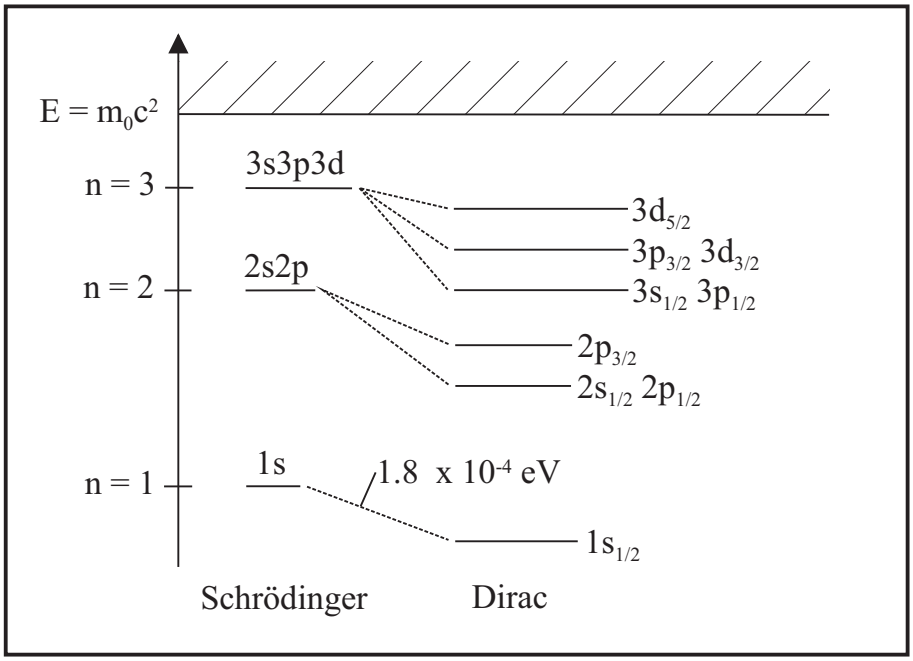


Figure 5.2: Energy spectrum of the Coulomb problem

Further corrections of energy spectrum:

- hyperfine structure (coupling of magnetic moments of electrons + nuclei) $\sim 10^{-6}$ eV
- QED effects ('Lamb shift') $\sim 10^{-6}$ eV

Instead of solving eqs. (5.15)-(5.17) exactly and subsequently expanding the solutions one can consider a 'weakly relativistic' limit of the stationary DE (5.15) and solve it in 1^{st} order perturbation theory. This procedure yields the result (5.18) once again, but together with some interpretations concerning the nature of the relativistic corrections.

One obtains

$$\hat{H}_{\mathbf{D}} \overset{v \ll c}{\approx} \hat{H}_{\text{Schrödinger}} + \hat{H}_1 + \hat{H}_2 + \hat{H}_3$$

with

$$\hat{H}_1 = -\frac{\hat{\boldsymbol{p}}^4}{8m^3c^2}$$

'mass-velocity' term $\longrightarrow$ corresponds to relativistic correction of non-relativistic kinetic energy

$$\hat{H}_2 = \frac{Ze^2}{8\pi\epsilon_0 m^2c^2} \cdot \frac{1}{r^3}(\hat{\mathbf{s}} \cdot \hat{\mathbf{l}})$$

'spin-orbit-coupling' $\longrightarrow$ a natural consequence of relativistic electron dynamics! (cf. chap. 4.3.3)

$$\hat{H}_3 = \frac{\hbar^2}{8m^2c^2}\Delta V_{Coulomb}(r) = \frac{Ze^2\hbar^2}{8m^2c^2\epsilon_0}\delta(\mathbf{r})$$

'Darwin term' $\longrightarrow$ 'Zitterbewegung'

(its appearance is connected with existence of negative energy solutions)

Appendix A

Some details

A.1 Details on the splitting at the potential well

$$\psi(x) = \begin{cases} e^{ik_1 x} + Be^{-ik_1 x} & I \\ Ce^{ik_2 x} + De^{-ik_2 x} & II \\ Ee^{ik_1 x} & III \end{cases}$$

$$\psi'(x) = \begin{cases} ik_1 e^{ik_1 x} - ik_1 Be^{-ik_1 x} & I \\ ik_2 Ce^{ik_2 x} - ik_2 De^{-ik_2 x} & II \\ ik_1 Ee^{ik_1 x} & III \end{cases}$$

matching conditions at $x = -\frac{L}{2}$:

$$\begin{array}{rl} \psi: & e^{-\frac{ik_1 L}{2}} + Be^{\frac{ik_1 L}{2}} = Ce^{-\frac{ik_2 L}{2}} + De^{\frac{ik_2 L}{2}} \\ \psi': & k_1 e^{-\frac{ik_1 L}{2}} - k_1 Be^{\frac{ik_1 L}{2}} = k_2 Ce^{-\frac{ik_2 L}{2}} - k_2 De^{\frac{ik_2 L}{2}} \end{array} \quad \cdot\frac{1}{k_1}$$

$$\xrightarrow{+} \quad 2e^{-\frac{ik_1 L}{2}} = C(1+\frac{k_2}{k_1})e^{-\frac{ik_2 L}{2}} + D(1-\frac{k_2}{k_1})e^{\frac{ik_2 L}{2}} \qquad |\cdot\frac{1}{2}e^{\frac{ik_1 L}{2}}$$

$$\iff \quad \boxed{\frac{1}{2}\Big\{C(1+\frac{k_2}{k_1})e^{\frac{i}{2}(k_1-k_2)L} + D(1-\frac{k_2}{k_1})e^{\frac{i}{2}(k_1+k_2)L}\Big\} = 1} \qquad (*)$$

matching conditions at $x = +\frac{L}{2}$:

$$\begin{array}{rl} \psi: & \left| \; Ce^{\frac{ik_2L}{2}} + De^{-\frac{ik_2L}{2}} = Ee^{\frac{ik_1L}{2}} \right. \\ \psi': & \left| \; k_2Ce^{\frac{ik_2L}{2}} - k_2De^{-\frac{ik_2L}{2}} = k_1Ee^{\frac{ik_1L}{2}} \right| \cdot\frac{1}{k_2} \end{array}$$

$$\xrightarrow{+} \quad 2Ce^{\frac{ik_2L}{2}} = E(1+\frac{k_1}{k_2})e^{\frac{ik_1L}{2}} \qquad | \cdot \frac{1}{2}e^{-\frac{ik_2L}{2}}$$

$$\Longleftrightarrow \quad \boxed{C = \frac{1}{2}E(1+\frac{k_1}{k_2})e^{\frac{i}{2}(k_1-k_2)L}} \qquad (**)$$

$$\xrightarrow{-} \quad \boxed{D = \frac{1}{2}E(1-\frac{k_1}{k_2})e^{\frac{i}{2}(k_1+k_2)L}} \qquad (***)$$

Insert (**) and (***) into (*):

$$\begin{aligned} 1 &= \frac{1}{2}\Big\{\frac{E}{2}(1+\frac{k_1}{k_2})(1+\frac{k_2}{k_1})e^{i(k_1-k_2)L} + \frac{E}{2}(1-\frac{k_1}{k_2})(1-\frac{k_2}{k_1})e^{i(k_1+k_2)L}\Big\} \\ &= \frac{E}{4}e^{ik_1L}\Big\{(2+\frac{k_1}{k_2}+\frac{k_2}{k_1})e^{-ik_2L} + (2-\frac{k_1}{k_2}-\frac{k_2}{k_1})e^{ik_2L}\Big\} \\ &= Ee^{ik_1L}\Big\{\cos(k_2L) - \frac{i}{2}(\frac{k_1}{k_2}+\frac{k_2}{k_1})\sin(k_2L)\Big\} \end{aligned}$$

$$\boxed{E = \frac{e^{-ik_1L}}{\cos(k_2L) - \frac{i}{2}\left(\frac{k_1}{k_2}+\frac{k_2}{k_1}\right)\sin(k_2L)}}$$

$$\boxed{T = |E|^2 = \frac{1}{\cos^2(k_2L) + \frac{1}{4}\left(\frac{k_1}{k_2}+\frac{k_2}{k_1}\right)^2\sin^2(k_2L)}}$$

A.2 Remarks on photoabsorption

Starting point for the discussion of the interaction of a hydrogen atom (chap. 4.4) and the EM-field

$$\begin{aligned}\hat{H} &= \frac{1}{2m}(\hat{\mathbf{p}}+e\mathbf{A})^2 - e\phi - \frac{Ze^2}{4\pi\varepsilon_0 r} \\ &= \underbrace{\frac{\hat{\mathbf{p}}^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r}}_{\hat{H}_0} + \underbrace{\frac{e}{2m}\Big(\hat{\mathbf{p}}\cdot\mathbf{A}+\mathbf{A}\cdot\hat{\mathbf{p}}\Big) + \frac{e^2}{2m}\mathbf{A}^2 - e\phi}_{\hat{V}(t)}\end{aligned}$$

monochromatic, sourcefree electromagnetic field can be characterized by vector potential in Coulomb gauge

$$\begin{aligned}\mathbf{A}(\mathbf{r},t) &= \mathbf{n}\Big(A_0 e^{i(\mathbf{kr}-\omega t)} + A_0^* e^{-i(\mathbf{kr}-\omega t)}\Big)\,, \qquad (k=\frac{\omega}{c}) \\ \boldsymbol{\nabla}\cdot\mathbf{A} &= 0 \implies (\mathbf{n}\perp\mathbf{k}) \\ \phi &= 0\end{aligned}$$

if $A^2 \ll A$

$$\begin{aligned}\hookrightarrow \quad \hat{H} &= \hat{H}_0 + \hat{V}(t) \\ \hat{V}(t) &= \frac{\hbar e}{2mi}(\boldsymbol{\nabla}\cdot\mathbf{A}+\mathbf{A}\cdot\boldsymbol{\nabla}) \\ &= \frac{\hbar e}{mi}\mathbf{A}(\mathbf{r},t)\cdot\boldsymbol{\nabla} \;=\; \frac{e}{m}\mathbf{A}\cdot\hat{\mathbf{p}} \qquad \text{(Coulomb gauge!)} \\ &= \frac{e}{m}A_0 e^{i(\mathbf{kr}-\omega t)}\mathbf{n}\cdot\hat{\mathbf{p}} + \frac{e}{m}A_0^* e^{-i(\mathbf{kr}-\omega t)}\mathbf{n}\cdot\hat{\mathbf{p}} \\ \overset{\text{cf. (4.49)}}{=} &\Big(\frac{e}{m}A_0^* e^{-i\mathbf{kr}}\mathbf{n}\cdot\hat{\mathbf{p}}\Big)e^{i\omega t} + \Big(\frac{e}{m}A_0 e^{i\mathbf{kr}}\mathbf{n}\cdot\hat{\mathbf{p}}\Big)e^{-i\omega t} \\ = &\qquad \hat{B} \qquad e^{i\omega t} + \qquad \hat{B}^\dagger \qquad e^{-i\omega t}\end{aligned}$$

$$p^{\text{abs}}_{o\to k} \;\propto\; |B^\dagger_{k0}|^2 = \frac{e^2}{m^2}|A_0|^2\;|\langle\varphi_k|e^{i\mathbf{kr}}\mathbf{n}\cdot\hat{\mathbf{p}}|\varphi_0\rangle|^2$$

transition matrix element

$$T_{k0} = \langle\varphi_k|e^{i\mathbf{kr}}\mathbf{n}\cdot\hat{\mathbf{p}}|\varphi_0\rangle$$

dipole approximation

$$e^{i\mathbf{kr}} = e^{\frac{\omega}{c}z} \approx 1\,, \qquad \text{justified for } k \ll a_0^{-1}$$

$\hookrightarrow$ dipole-velocity form of the transition matrix element

$$T^{\text{Dip}}_{k0} = \langle\varphi_k|\mathbf{n}\cdot\hat{\mathbf{p}}|\varphi_0\rangle$$

use commutation relation $\hat{\mathbf{p}} = \frac{im}{\hbar}[\hat{H}_0, \hat{\mathbf{r}}]$

$$\begin{aligned} \hookrightarrow \quad T_{k0}^{\mathrm{Dip}} &= \frac{im}{\hbar}\langle\varphi_k|\hat{H}_0\mathbf{n}\cdot\hat{\mathbf{r}} - \mathbf{n}\cdot\hat{\mathbf{r}}\hat{H}_0|\varphi_0\rangle \\ &= \frac{im}{\hbar}(\varepsilon_k - \varepsilon_0)\langle\varphi_k|\mathbf{n}\cdot\hat{\mathbf{r}}|\varphi_0\rangle \qquad \mathrm{dipole-length\ form} \\ &= im\omega\langle\varphi_k|\mathbf{n}\cdot\hat{\mathbf{r}}|\varphi_0\rangle \end{aligned}$$

$\hat{H}_0$ is a central-field problem for the hydrogen atom

$$\hookrightarrow \quad \varphi_j(\mathbf{r}) = R_j(r)Y_{l_j m_j}(\Omega)$$

choose $\mathbf{n} = \mathbf{e}_z \quad \hookrightarrow \quad \mathbf{n}\cdot\mathbf{r} = z = r\cos\theta = \sqrt{\frac{4\pi}{3}}rY_{10}$

$$\hookrightarrow \quad T_{k0}^{\mathrm{Dip}} = \sqrt{\frac{4\pi}{3}}im\omega\int_0^\infty r^3 R_k(r)R_0(r)\int Y^*_{l_k m_k}(\Omega)Y_{10}(\Omega)Y_{l_0 m_0}(\Omega)\ d\Omega$$

The angular integral over 3 spherical harmonics is a well-known special case of the so-called Wigner-Eckart theorem. It is nonzero only if

$$m_k = m_0 \quad \wedge \quad |l_k - l_0| = 1$$

(dipole) 'selection rules'

Literature: [Mes] QM II, Appendix C; [Lin]
For $\varphi_0 = \varphi_{1s}(r)$

$\longrightarrow$ possible transitions $1s \longrightarrow 2p_0, 3p_0, \ldots\ (E < 0)$
and continuum states with $l = 1$

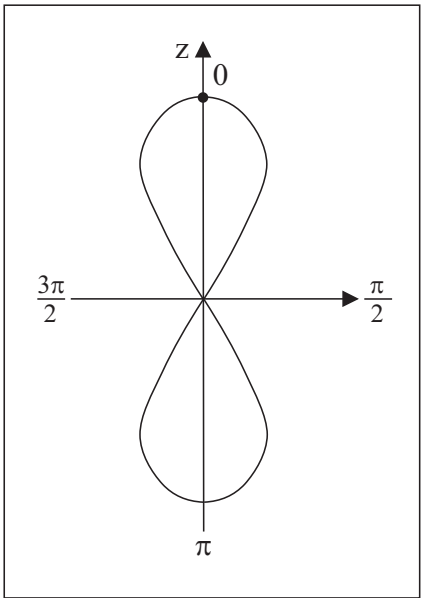


Figure A.1: dipole characteristic $\cos^2\theta$ dependence

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