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## The Schrödinger equation as a wave equation

- Schrödinger equation
- Box potential
- Harmonic oscillator
- Orbital angular momentum
- Rotation of a diatomic molecule
- Schrödinger equation of the H-atom
- normal Zeeman effect
- Dia- and paramagnetism



Revision

# Orbital angular momentum 1

Johannes Kepler (1609): Planets move in elliptical orbits



Newton defines the orbital angular momentum

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

Newton's mechanics: the angular momentum is conserved and perpendicular to the plane of the orbit of a planet

$$\frac{d\vec{L}}{dt}=0$$

Comment 1

# Orbital angular momentum 1

In 1609 Johannes Kepler published his findings on the movement of the planets.

Planets move in elliptical orbits around the sun.

A line segment joining a planet and the Sun sweeps out equal areas during equal intervals of time.

The squares (second powers) of the orbital times of two planets around the same central star behave like the cubes (third powers) of the major orbital half-axes.

Newtonian mechanics explains Kepler's laws.

In particular, Newton defines the orbital angular momentum, which is indicated by the formula underlined in red.



According to its definition, the orbital angular momentum is perpendicular to the plane of the orbit and does not change during the movement of the planet.

With a central force such as gravitational force, the derivative of the orbital angular momentum with respect to time must always be zero.

The time derivative of the position vector gives the speed, which is parallel to the momentum, so that the cross product must be zero.

The time derivative of the momentum is the force that, due to the law of gravitation, is parallel to the position vector that connects the sun with the planet, so that the cross product must also be zero here.

According to the uncertainty relations, there can be no orbital plane for a quantum particle, i.e.  $\frac{d\vec{L}}{dt} \neq 0$ 

One can begin the discussion of angular momentum in quantum physics with the uncertainty relation for the orbital angular momentum

$$\Delta \varphi \Delta L_z \geq rac{\hbar}{2}$$



According to the uncertainty relations, a quantum particle cannot move in an orbital plane.

Hence the angular momentum in quantum physics cannot be independent of time.

A first access to the properties of the orbital angular momentum in quantum physics is provided by the uncertainty relation outlined in red.

uncertainty relation

$$\Delta x \Delta p_x \geq rac{\hbar}{2}$$

motion in the x-y plane

$$\frac{\Delta x}{r}r\Delta p_{x}\geq \frac{\hbar}{2}$$

With  $\Delta x/r = \Delta \varphi$  and  $r \Delta p_x = \Delta L_z$ 

$$\Delta \varphi \Delta L_z \geq rac{\hbar}{2}$$

uncertainty relation of the angular momentum



Comment 1

The formulas and pictures on this page should make the uncertainty relation for the angular momentum plausible.

The first line shows the uncertainty relation in the x-direction.

The first figure on the right shows the momentum and the momentum uncertainty in the x-direction for a particle.

The distance of a point to the origin of the coordinates is denoted by *r*.

The quotient of the position uncertainty  $\Delta x$  and the distance *r* gives the uncertainty of the angle  $\varphi$ .

### Comment 2

The product of the distance *r* and the uncertainty of the momentum  $\Delta p_x$  is a contribution to the orbital angular momentum in the *z*-direction.

This results in the uncertainty for the orbital angular momentum component in the z-direction.

The uncertainty in the angle  $\Delta \varphi$  and the uncertainty in the *z*-component of the orbital angular momentum give the uncertainty relation of the orbital angular momentum.

The second figure on the right shows the angular momentum vector.

The orientation of the angular momentum vector is determined by the angle  $\varphi$  and the angle  $\theta$ .



If the angle  $\varphi$  cannot be determined because of the uncertainty relation, then the xand y-components of the angular momentum can no longer be determined either.

This is shown in the following illustration

When  $\Delta L_z = 0$  follows  $\Delta \phi \rightarrow \infty$  and

 $L_x$  and  $L_y$  are not defined



it turns out that in addition to  $L_z$  also  $|\vec{L}|$  can be fixed

Comment

If the z-component of the orbital angular momentum has a fixed value, i.e. the uncertainty  $\Delta L_z$  is zero, then the uncertainty of the associated angle  $\varphi$  is infinite.

This means that it is no longer possible to assign fixed values to the x and y components of the orbital angular momentum.

As will be shown below, the length of the angular momentum vector is still defined.

The figure shows the vector representation of angular momentum in quantum physics.

The vector of the angular momentum lies on a conical surface around the z-axis.

However, the exact position of the angular momentum vector on this conical surface is not determined.

the operator of the orbital angular momentum

$$\vec{L} = \vec{r} \times \vec{p} \quad \rightarrow \quad \hat{\vec{L}} = \vec{r} \times (-i\hbar)\nabla$$

z-component of the angular momentum operator

$$\hat{\rho}_{x} = -i\hbar rac{\partial}{\partial x} \quad 
ightarrow \qquad \hat{L}_{z} = -i\hbar rac{\partial}{\partial \varphi}$$

compare

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad \rightarrow \quad \Delta \varphi \Delta L_z \geq \frac{\hbar}{2}$$

### Comment 1

In order to find the contained components of the angular momentum, one has to find the eigenvalue equations of the angular momentum according to the rules of quantum mechanics.

In classical mechanics, the orbital angular momentum is defined by the cross product of position and momentum vector.

The operator of the orbital angular momentum results when the momentum is replaced by the momentum operator.

The first equation outlined in red gives the angular momentum operator.

All properties of angular momentum can be determined by analyzing this operator.

However, this procedure leads to complex calculations, which are not worth to be discussed in a lecture (for details see books of Quantum Mechanics).

#### Comment 2

Usually the angular momentum operator is not expressed in Cartesian coordinates, but in spherical coordinates  $\theta$  and  $\varphi$ .

The z-component of the angular momentum operator results in a formula that corresponds to the formula of the momentum operator.

If one compares the uncertainty relations for momentum and orbital angular momentum, one recognizes that the coordinate *x* corresponds to the angle  $\varphi$  and the momentum  $p_x$  corresponds to the *z*-component of the orbital angular momentum  $L_z$ .

With simple replacement, the formula for the momentum operator results in the formula outlined in red for the z-component of the angular momentum operator.

This result can also be obtained if one strictly adheres to the rules of mathematics.

eigenvalue equation of  $\hat{L}_z$ 

$$\hat{L}_{z}f(\boldsymbol{\varphi})=-i\hbarrac{\partial}{\partial \boldsymbol{\varphi}}f(\boldsymbol{\varphi})= ext{eigenvalue}\cdot f(\boldsymbol{\varphi})$$

eigenfunctions

$$\underline{f(\boldsymbol{\varphi})} = \mathbf{e}^{im\boldsymbol{\varphi}}$$

$$f(\boldsymbol{\varphi}) = f(\boldsymbol{\varphi} + 2\pi) \quad \rightarrow \quad \boldsymbol{m} = 0, \pm 1, \pm 2, \dots$$



The first line gives the formal definition of the eigenvalue equation.

The operator applied to the wave function gives the eigenvalue times the wave function.

The solution of this differential equation is simply the complex exponential function.

The quantum number *m* has the integer values  $m = 0, \pm 1, \pm 2, ...$ 

This must be so, because adding a multiple of  $2\pi$  to the argument of the complex exponential function cannot change the value of the function.

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eigenvalue equation of \hat{L}_z
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\hat{L}_{z}f_{m}(oldsymbol{arphi})=m\hbar f_{m}(oldsymbol{arphi})
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quantum numbers of  $\hat{L}_z$ 

 $m = 0, \pm 1, \pm 2, ...$ 

eigenfunctions of  $\hat{L}_z$ 

```
f_m(\varphi) = e^{im\varphi}
```

eigenvalues of  $\hat{L}_z$ 

 $L_z = m\hbar$ 

The slide summarizes the results.

The equation outlined in red gives the eigenvalue equation of  $\hat{L}_z$ .

The quantum numbers of  $\hat{L}_z$  are  $m = 0, \pm 1, \pm 2, ...$ 

The eigenfunctions are the complex exponential functions and the eigenvalues of the z-component of the angular momentum are  $m\hbar$ .

The z-component of the angular momentum is conserved and takes on the values  $m\hbar$ .



the length of the angular momentum vector





Only the z-component of the angular momentum operator has so far been determined by an eigenvalue equation.

The x and y components of the angular momentum operator cannot have fixed values.

What about the length of the angular momentum vector?

To find the eigenvalue equation for the absolute value of the angular momentum vector, I use a little trick.



$$\vec{L} = \vec{r} imes \vec{p} = \vec{r} imes \vec{p}_r + \vec{r} imes \vec{p}_t = rp_t \vec{e}_z$$

kinetic energy

$$E_{kin} = \frac{\vec{p}^2}{2m} = \frac{\vec{p}_r^2}{2m} + \frac{\vec{p}_t^2}{2m} = \frac{\vec{p}_r^2}{2m} + \frac{r^2 \vec{p}_t^2}{2mr^2} = \frac{\vec{p}_r^2}{2m} + \frac{\vec{L}^2}{2mr^2}$$



The figure shows a particle moving in the xy-plane.

The momentum of the particle can be broken down into a component parallel to the position vector, which connects the particle with the origin of the coordinate system, and into a component perpendicular to the position vector.

The angular momentum of the particle is perpendicular to the xy plane and is determined by the transverse momentum  $p_{t}$ .

The kinetic energy is proportional to the square of the momentum.

A small calculation shows that the kinetic energy is given by the kinetic energy in the radial direction and the kinetic energy of a rotation, which is proportional to the square of the angular momentum.



Laplace Operator in spherical coordinates (https://en.wikipedia.org/wiki/Laplace\_operator)

$$\nabla^{2} = \frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial y^{2}} + \frac{\partial^{2}}{\partial z^{2}}$$
$$= \frac{1}{r^{2}}\frac{\partial}{\partial r}\left(r^{2}\frac{\partial}{\partial r^{2}}\right) + \frac{1}{r^{2}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^{2}\theta}\frac{\partial^{2}}{\partial\varphi^{2}}\right\}$$



The first formula outlined in red gives the Hamilton operator of the kinetic energy.

The Hamilton operator contains the square of Nabla, which is also known as the Laplace operator.

In the second area outlined in red, the first line specifies the Laplace operator in Cartesian coordinates.

The second line gives the Laplace operator in spherical coordinates.

Hamilton operator of the classical kinetic energy

$$\hat{H} = rac{\hat{ec{p}}^2}{2m} = -rac{\hbar^2 
abla^2}{2m}$$
 and  $E_{kin} = rac{ec{p}_r^2}{2m} + rac{ec{L}^2}{2mr^2}$ 

Laplace operator in spherical coordinates

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

operator of the square of the angular momentum

$$\hat{\vec{L}}^2 = -\hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right\}$$



The first line gives the Hamilton operator of the kinetic energy and the decomposition of the kinetic energy into a radial component and a component that is related to the rotation of the mass *m*.

The second line gives the Laplace operator in spherical coordinates.

The comparison shows that the Hamilton operator of the kinetic energy can also be broken down into the radial contribution and a contribution that corresponds to a rotation.

The comparison results in the operator for the square of the orbital angular momentum, which is outlined in red in the bottom line.

eigenvalue equation of the square of the angular momentum

$$\hat{\vec{L}}^2 Y_{\ell,m}(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y_{\ell,m}(\theta,\varphi)$$

the eigenfunctions are spherical harmonics  $Y_{\ell,m}(\theta, \varphi)$ 

and the eigenvalues

$$L^2 = \ell(\ell+1)\hbar^2$$

the quantum numbers  $\ell$  and m are

$$\ell = 0, 1, 2, ...$$
 and  $|m| \le \ell$ 

The solutions to the eigenvalue equation for the angle-dependent part of the Laplace operator are known.

The equation outlined in red shows the eigenvalue equation for the square of the angular momentum.

The eigenfunctions are spherical harmonics, which will be discussed later.

The equation underlined in red gives the eigenvalues for the square of the angular momentum operator.

The eigenvalues are determined by the quantum number  $\ell$ .

The quantum number  $\ell$  takes on the values 0, 1, 2, etc.

### Comment 1



The spherical harmonics also depend on the quantum number *m*, since  $\vec{L}^2$  contains the square of the z-component  $L_z$ .

The quantum number *m* takes the integer values between  $-\ell$  and  $+\ell$ .





The figure shows the vectors of angular momentum for the quantum number  $\ell = 1$  and  $\ell = 2$ .

The length of the vector is  $\hbar \sqrt{\ell(\ell+1)}$ .

The vectors lie on conical surfaces, the edge of which is indicated by the blue circles.

Due to the uncertainty relation for the angular momentum, it is not possible to define the orientation of the vectors more precisely.

Revision

### Orbital angular momentum 14

#### eigenfunctions of the angular momentum operators

 $\underline{Y_{\ell,m}(\theta,\varphi)} = P_{\ell,m}(\theta) e^{im\varphi}$ 

- the  $e^{im\varphi}$  are the eigenfunctions of  $\hat{L}_z$
- **P\_{\ell,m}(\theta)** is a polynomial that is formed from sin  $\theta$  and cos  $\theta$  functions
- the  $Y_{\ell,m}(\theta, \varphi)$  are the eigenfunctions of  $\hat{L}_z$  and  $\hat{\vec{L}}^2$

 $\hat{\boldsymbol{L}}_{\boldsymbol{z}} \boldsymbol{Y}_{\ell,m}(\boldsymbol{\theta}, \boldsymbol{\varphi}) = \boldsymbol{m} \boldsymbol{h} \boldsymbol{Y}_{\ell,m}(\boldsymbol{\theta}, \boldsymbol{\varphi})$  $\hat{\boldsymbol{L}}^{2} \boldsymbol{Y}_{\ell,m}(\boldsymbol{\theta}, \boldsymbol{\varphi}) = \boldsymbol{\ell} (\boldsymbol{\ell} + 1) \boldsymbol{h}^{2} \boldsymbol{Y}_{\ell,m}(\boldsymbol{\theta}, \boldsymbol{\varphi})$ 



The spherical harmonics are the eigenfunctions of the angular momentum.

The spherical harmonics are formed by the product of the eigenfunctions of  $\hat{L}_z$ , i.e.  $e^{im\varphi}$ , and a polynomial that is formed from the sine and cosine functions of the angle  $\theta$ .

The formulas outlined in red give the eigenvalue equations of the two angular momentum operators  $\hat{L}_z$  and  $\hat{\vec{L}}^2$ .

ł	m	$P_{\ell,m}(\theta)$	
0	0	$\propto$ 1	
1	0	$\propto \cos  heta$	
1	±1	$\propto {\sf sin} {m  heta}$	(https://en.wikipedia.org/wiki/Table_of_spherical_harmonics)
2	0	$\propto 3\cos^2 heta-1$	
2	±1	$\propto \sin  heta \cos  heta$	
2	±2	$\propto \sin^2  heta$	

the spherical harmonics are normalized

$$\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\sin\theta d\theta d\varphi \mathsf{Y}_{\ell,m}\mathsf{Y}_{\ell,m}^{*}=\mathsf{1}$$



The table lists the most important spherical harmonics that are used in atomic physics.

Further information on spherical harmonics can be found on the specified www page.

The spherical harmonics are normalized functions.

The integral underlined in red gives the normalization condition.

only a small number of eigenfunctions of the orbital angular momentum are necessary in atomic physics

s:  $\ell = 0$ , p:  $\ell = 1$ , d:  $\ell = 2$ , f:  $\ell = 3$ , ...

s orbital ( $\ell = 0$  and m = 0)

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$



The spherical harmonics with the quantum numbers  $\ell = 0, 1, 2$  and 3 are particularly important.

The solution of the Schrödinger equation for hydrogen atom (discussed later) shows that these angular momentum states should be denoted by the letters s  $(\ell = 0)$ , p  $(\ell = 1)$ , d  $(\ell = 2)$  and f  $(\ell = 3)$ .

If the angular momentum is zero then the quantum numbers are  $\ell = 0$  and m = 0.

The eigenfunction is  $Y_{00}$  is simply a constant since all differentiations with respect to  $\theta$  and  $\varphi$  are zero.

The normalization factor is equal to  $\frac{1}{\sqrt{4\pi}}$  since the integration over  $\theta$  and  $\varphi$  results in the surface of the unit sphere 4  $\pi$ .

p orbitals ( $\ell = 1$  and  $m = 0, \pm 1$ )

 $p_z$  orbital (m = 0)





Comment

#### Orbital angular momentum 17

The  $p_z$  orbital is proportional to  $\cos\theta$ .

It is called  $p_z$ -orbital, since  $\cos \theta$  in spherical coordinates is the projection of a unit vector onto the z-axis.

The figure shows how the orbital is visualized.

To do this, the area is drawn on which the vectors with the length  $|Y_{\ell,m}(\theta, \varphi)|$  for the different spatial directions end.

The figure shows the intersections of this surface with the xy plane.

 $p_x$  and  $p_y$  orbitals ( $m = \pm 1$ )

$$\mathsf{Y}_{1,\pm 1}\propto \sin heta\,\mathsf{e}^{\pm\mathrm{i}arphi}=\sin heta\,\cosarphi\pm\mathsf{i}\,\sin heta\,\sinarphi$$

the p<sub>x</sub> orbital is the real part of Y<sub>1,±1</sub>, i.e. ∝ sin θ cos φ ∝ x
 the p<sub>y</sub> orbital is the imaginary part of Y<sub>1,±1</sub>, i.e. ∝ sin θ sin φ ∝ y





The real and imaginary part of  $Y_{1,\pm 1}$  are called  $p_x$  and  $p_y$  orbitals.

The figure shows an illustration of the  $p_x$ ,  $p_y$ , and  $p_z$  orbital.

These orbitals have the same shape because they can be transformed into one another by rotating the coordinate axes.

d orbitals  $\ell$  = 2 and m = 0, ±1, ±2

 $d_{3z^2-1}$  orbital (m = 0)

 $Y_{20} \propto (3\cos^2\theta - 1)$ 



for 
$$\theta_m = 54.74^\circ$$
:  $3\cos^2\theta_m - 1 = 0$ 



- For  $\ell = 2$  there are 5 eigenfunctions.
- The figure shows  $Y_{00}$ .

The length of the vectors that define the surface is  $|3\cos^2\theta - 1|$ .

 $Y_{00}$  is called the  $d_{3z^2-1}$  orbital since  $\cos\theta \propto z$ .

#### all d orbitals

$$\begin{array}{ll} Y_{2,0} & \propto 3\cos^2\theta - 1 & \propto 3z^2 - 1 \\ Y_{2,\pm 1} & \propto \sin\theta\cos\theta e^{\pm i\varphi} & \propto xz \pm iyz \\ Y_{2,\pm 2} & \propto \sin^2\theta e^{\pm 2i\varphi} & \propto x^2 - y^2 \pm i2xy \end{array}$$



spherical coordinates

$$\rightarrow$$
  $d_{3z^2-1}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{x^2-y^2}$ ,  $d_{xy}$  orbitals



The formulas outlined in red indicate the spherical surface functions for all *d* orbitals with the decomposition into real and imaginary parts.

The sine and cosine functions are replaced by the projection of a unit vector onto the x, y and z axes.

This results in the usual designation of this orbital as  $d_{3z^2-1}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{x^2-y^2}$ , and  $d_{xy}$  orbitals.



(Drehimpulsorbitale.mp4)



Most *d* orbitals have a cloverleaf shape.

The video gives a spatial impression of these orbitals.

# **Diatomic Molecule**

# The Schrödinger equation as a wave equation

- Schrödinger equation
- Box potential
- Harmonic oscillator
- Orbital angular momentum
- Rotation of a diatomic molecule
- Schrödinger equation of the H-atom
- normal Zeeman effect
- Dia- and paramagnetism

rotation of a point mass

$$E_{rot} = rac{ec{L}^2}{2mr^2}$$

rotation of a diatomic molecule

$$E_{rot} = \frac{\vec{L}^2}{2I}$$

moment of inertia  $I = \sum_{i=1,2} m_i r_i^2$ 

$$E_{rot} = \frac{\ell(\ell+1)\hbar^2}{2I} \quad \rightarrow \quad E_{rot} = B\ell(\ell+1)$$

Comment 1

# Rotation of a diatomic molecule 1

The angular momentum quantization can be observed directly in the rotational spectra of diatomic molecules in the gas phase.

The first formula underlined in red gives the rotational energy for a particle of mass m at a distance r from the axis of rotation.

In the case of a molecule, the moment of inertia *I* must be used instead of the mass *m*.

In general there are three principal orthogonal axes of rotation.

In the case of a diatomic molecule, only rotations perpendicular to the molecular axis can be excited.

This results in the second formula underlined in red.

In the formula for the moment of inertia,  $r_{i=1,2}$  denotes the distance between the two atoms and the center of gravity of the molecule.

With the rotational energy, the Hamilton operator for the rotation of the molecule results when the angular momentum is replaced by the angular momentum operator.

The eigenfunctions of the time-independent Schrödinger equation are the spherical harmonics.

The formula outlined in red shows the energy eigenvalues of the time-independent Schrödinger equation.

The energy is quantized and proportional to  $\ell(\ell + 1)$ .

#### Comment 2

 $E_{rot} = B\ell(\ell + 1)$ 



The figure shows the expected energy level scheme for the rotation of a diatomic molecule.

For electric dipole radiation, the Schrödinger equation yields the selection rule  $\Delta \ell = \pm 1$ .

With this selection rule, the red marked transitions between the energy levels result.

The transition energy of the radiation increases in steps of  $2B = \hbar^2/I$ .



#### microwave spectrum of the CO molecule



Comment 1

# Rotation of a diatomic molecule 3

The figure shows the microwave spectrum of carbon monoxide.

The experimental observations confirm the theoretical results.

The intensity of the transitions is determined on the one hand by the transition probability, which increases with increasing values of the quantum number  $\ell$ .

On the other hand, the thermal occupation of the energy levels must be taken into account.

The intensity of the spectral lines increases on the left side of the spectrum due to the increasing transition probability (increasing  $\ell$  quantum number) and decreases due to the thermal occupation of the energy levels on the right side of the spectrum.



With the distance between the spectral lines of about 116 GHz, the moment of inertia of carbon monoxide and from this the distance between the two atoms can be determined.

# Revision

# Summary in Questions 1

- 1. Sketch the vector of the quantized angular momentum and justify the sketch.
- 2. Give the length of the z-component of the quantized angular momentum.
- 3. Give the length of the quantized angular momentum vector.
- 4. Give the eigenvalue equations of the angular momentum operator.
- 5. Spherical harmonics are the eigenfunctions of the angular momentum operator. Explain the structure of the spherical harmonics.
- 6. Give the formulas of the spherical harmonics  $Y_{1,-1}$ ,  $Y_{1,0}$  and  $Y_{1,+1}$  without the normalization factor.
- 7. Give the energy eigenvalues for the rotation of a diatomic molecule.

# Summary in Questions 2

- 8. Calculate the energy difference  $E_{\ell+1} E_{\ell}$ .
- 9. Show that  $\cos \theta$  is an eigenfunction of the angular momentum operators and determine the quantum number  $\ell$  and *m*.