Evaluation

- Lecture

  https://onlineumfrage.kit.edu/evasys/online.php?p=REGWV

Atoms

Orbital angular momentum

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

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 $\hat{L}_z$
- $P_{\ell,m}(\theta)$ are polynomials that are formed from $\sin\theta$ and $\cos\theta$ functions
- the $Y_{\ell,m}(\theta,\varphi)$ are the eigenfunctions of $\underline{\hat{L}_z \text{ and } \hat{\vec{L}}^2}$

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

Orbital angular momentum 14 Comment

The spherical harmonics are the eigenfunctions of the angular momentum.

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

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

Orbital angular momentum 15

the spherical harmonics are normalized

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

$Y_{\ell,m}Y_{\ell,m}^{*}$ gives the probability that the position vector $\vec{r}$ of a particle points in the direction θ and φ.

Orbital angular momentum 15 Comment

The spherical harmonics are normalized functions.

The integral underlined in red gives the normalization condition.

The position $\vec{r}$ of a particle in spherical coordinates is described by the coordinates r, θ and φ.

$Y_{\ell,m} Y_{\ell,m}^{*}$ is the probability that the vector $\vec{r}$ points in the direction indicated by the angles θ and φ.

Orbital angular momentum 16

ℓ	m	$P_{\ell,m}(\theta)$
0	0	$\propto 1$
1	0	$\propto \cos\theta$
1	± 1	$\propto \sin\theta$
2	0	$\propto 3\cos^2\theta - 1$
2	± 1	$\propto \sin\theta\cos\theta$
2	± 2	$\propto \sin^2\theta$

(https://en.wikipedia.org/wiki/Table_of_spherical_harmonics)

Orbital angular momentum 16 Comment

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.

Orbital angular momentum 17

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 $m = 0$)

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

Orbital angular momentum 17 Comment

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

The comparison with the optical spectra of the atoms shows that we denote the eigenstates of the angular momentum with letters s ($\ell = 0$), p ($\ell = 1$), d ($\ell = 2$) and f ($\ell = 3$), etc., to preserve the notations used in the era before the Schrödinger equation.

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 θ and φ are zero.

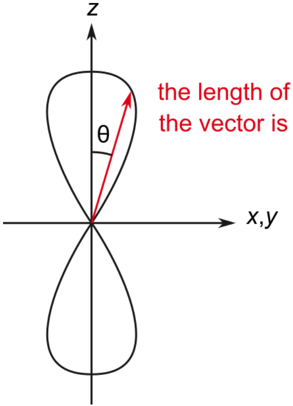
The normalization factor is equal to $\frac{1}{\sqrt{4\pi}}$ since the integration over θ and φ results in the surface of the unit sphere 4 π.

Orbital angular momentum 18

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

p_z orbital ($m = 0$)

$$Y_{1,0} \propto \cos\theta$$



the length of the vector is cosθ

Orbital angular momentum 18 Comment

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.

One simply draws the endpoints of a vector of length $|Y_{\ell,m}(\theta,\varphi)|$ for the different angles θ and φ. Sometimes the sign of $Y_{\ell,m}(\theta,\varphi)$ is indicated by color.

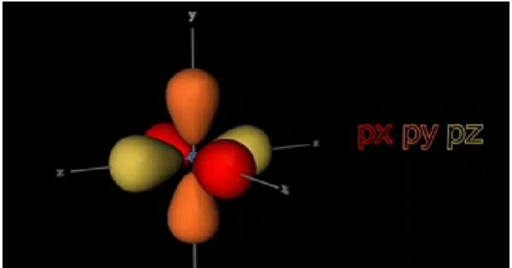
The figure shows the intersections of the resulting surface with the xy plane.

Orbital angular momentum 19

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

$$Y_{1,\pm 1} \propto \sin\theta\, e^{\pm i\varphi} = \sin\theta\cos\varphi \pm i\sin\theta\sin\varphi$$

- the $\mathrm{p_x}$ orbital is the real part of $Y_{1,\pm 1}$, i.e. $\propto \sin\theta\cos\varphi \propto x$
- the $\mathrm{p_y}$ orbital is the imaginary part of $Y_{1,\pm 1}$, i.e. $\propto \sin\theta\sin\varphi \propto y$



Orbital angular momentum 19 Comment

The real and imaginary part of $Y_{1,\pm1}$ are called $\mathrm{p_x}$ and $\mathrm{p_y}$ orbitals.

The figure shows an illustration of the $\mathrm{p_x}$, $\mathrm{p_y}$, and $\mathrm{p_z}$ orbital.

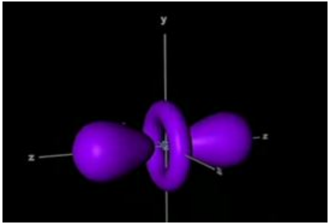
These orbitals have the same shape because they can be transformed into one another by rotating the coordinate axes.

Orbital angular momentum 20

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

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

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



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

Orbital angular momentum 20 Comment

For $\ell = 2$ there are 5 eigenfunctions.

The figure shows Y_{20}.

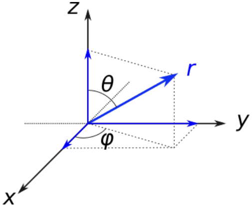
The length of the vectors that define the surface is $|3\cos^2\theta - 1|$.

Y_{20} is called the d_{3z^2-1} orbital since $\cos\theta \propto z$.

Orbital angular momentum 21

all *d* orbitals

$$\boxed{\begin{array}{lll} Y_{2,0} & \propto 3\cos^2\theta - 1 & \propto 3z^2 - 1 \\ Y_{2,\pm1} & \propto \sin\theta\cos\theta\, e^{\pm i\varphi} & \propto xz \pm iyz \\ Y_{2,\pm2} & \propto \sin^2\theta\, e^{\pm 2i\varphi} & \propto x^2 - y^2 \pm i2xy \end{array}}$$



spherical coordinates

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

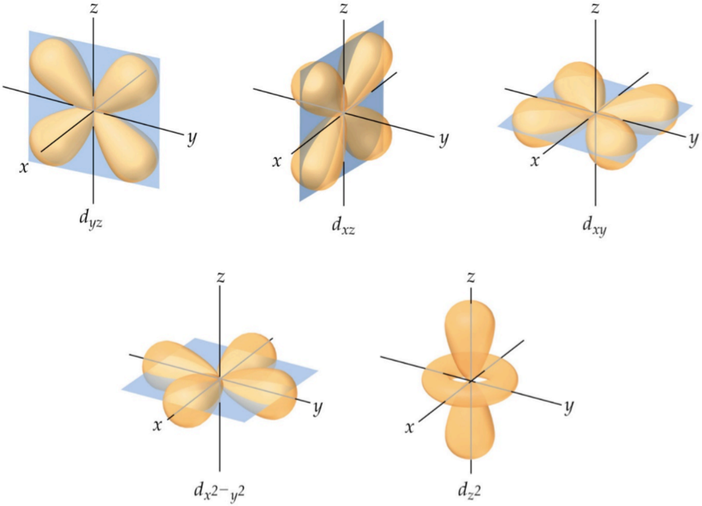
Orbital angular momentum 21 Comment

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}, $\mathrm{d}_{x^2-y^2}$, and d_{xy} orbitals.

Orbital angular momentum 22



(Drehimpulsorbitale.mp4)

Orbital angular momentum 22 Comment

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

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Rotation of a diatomic molecule 1

rotation of a point mass

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

rotation of a diatomic molecule

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

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

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

(Video: Rotation around the axes of inertia: Hauptträgheitsachsen.mp4)

Rotation of a diatomic molecule 1 Comment 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 general there are three principal orthogonal axes of rotation and the video shows that free rotation can be complicated.

In the case of a diatomic molecule, only rotations perpendicular to the molecular axis can be excited. Since all axes perpendicular to the molecular axis are identical, there is only one type of rotation.

This results in the second formula underlined in red.

Rotation of a diatomic molecule 1 Comment 2

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.

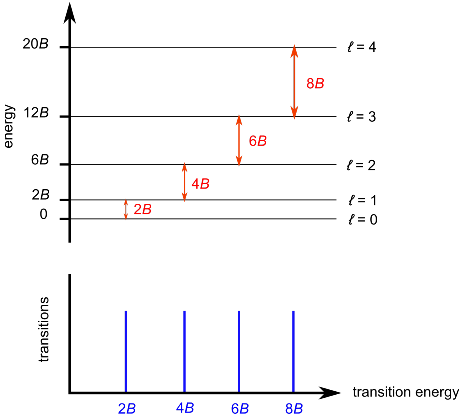
The eigenfunctions of the time-independent Schrödinger equation are the spherical harmonics.

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

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

Rotation of a diatomic molecule 2

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



Rotation of a diatomic molecule 2 Comment

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

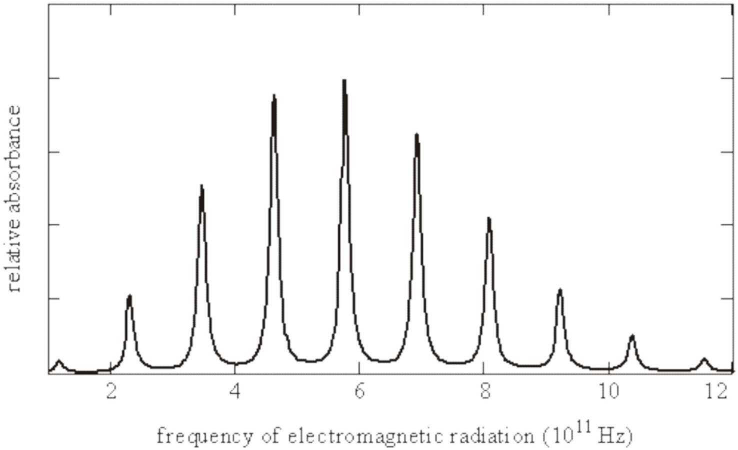
For electric dipole radiation, the Schrödinger equation yields the selection rule $\Delta\ell = \pm 1$.

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

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

Rotation of a diatomic molecule 3

microwave spectrum of the CO molecule



Rotation of a diatomic molecule 3 Comment 1

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 ℓ.

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 ℓ quantum number) and decreases due to the thermal occupation of the energy levels on the right side of the spectrum.

Rotation of a diatomic molecule 3 Comment 2

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.

Final remark about the eigenfunction of the angular momentum operators $Y_{\ell,m}(\theta,\varphi)$: For a diatomic molecule the two atoms can be replaced by one particle with the reduced mass $\mu^{-1} = m_1^{-1} + m_2^{-1}$.

The motion of the molecule is equivalent to the motion of the reduced mass at the distance r from the axis of rotation.

r corresponds to the distance between the two atom and $Y_{\ell,m} Y_{\ell,m}^*$ is the probability that the vector $\vec{r}$ points in the direction indicated by the angles θ and φ.

Hydrogen atom

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Schrödinger equation of the hydrogen atom 1

the hydrogen atom consists of an electron bound to a proton

Hamilton function

$$\underline{H = \frac{\vec{p}^{\,2}}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$

Hamilton operator $(\vec{p} \rightarrow -i\hbar\nabla)$

$$\boxed{\hat{H} = -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$

Schrödinger equation

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

Schrödinger equation of the hydrogen atom 1 Comment

The underlined equation gives the Hamilton function of a classical particle with potential energy.

The potential energy of the electron is caused by the electric field of the proton.

The Hamilton operator results when the momentum in the Hamilton function is replaced by the momentum operator $-\mathrm{i}\hbar\nabla$.

The equation in the bottom line shows the Schrödinger equation again.

Schrödinger equation of the hydrogen atom 2

Ansatz to solve the time-dependent Schrödinger equation

$$\underline{\psi(\vec{r}, t) = \varphi(\vec{r}\,) e^{-iEt/\hbar}}$$

time independent Schrödinger equation

$$\boxed{E\varphi(\vec{r}) = \hat{H}\varphi(\vec{r})}$$

the potential energy is only a function of the radius *r*

$$\hat{H} = -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

→ spherical coordinates for the Laplace operator

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

(https://de.wikipedia.org/wiki/Laplace-Operator)

Schrödinger equation of the hydrogen atom 2 Comment

Since the Hamilton operator does not explicitly contain the time, the solution of the Schrödinger equation is a standing wave.

The equation underlined shows the standing wave. The spatial and temporal variations are described by different functions.

This results in the time-independent Schrödinger equation.

Spherical coordinates can be used for the Laplace operator, since the potential energy of the electron only depends on the distance r to the atomic nucleus, i.e. to the proton.

Schrödinger equation of the hydrogen atom 3

$$
\begin{aligned}
\hat{H} &= -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \\
&= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \\
&\quad + \frac{1}{2mr^2}(-\hbar^2)\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \\
&\quad - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}
\end{aligned}
$$

Eigenvalue equation of the angular momentum operator

$$
\hat{\vec{L}}^2 Y_{\ell,m}(\theta,\varphi) = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\ell,m}(\theta,\varphi) = \hbar^2\ell(\ell+1)\,Y_{\ell,m}(\theta,\varphi)
$$

Schrödinger equation of the hydrogen atom 3 Comment

The Hamilton operator can thus be broken down into a radial and an angle-dependent part.

The angle-dependent part is determined by the square of the angular momentum.

This contribution is marked in blue in the equation outlined in red.

The last line gives the eigenvalue equation for the square of the angular momentum.

The eigenfunctions of the squared angular momentum operator are the spherical harmonics $Y_{\ell,m}(\theta,\varphi)$ and the ℓ quantum number takes on the values 0, 1, 2 etc. .

Schrödinger equation of the hydrogen atom 4

time independent Schrödinger equation of the hydrogen atom

$$E\varphi(\vec{r}) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\vec{L}}^2}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right)\varphi(\vec{r})$$

ansatz for the wave function

$$\varphi(\vec{r}) \quad \rightarrow \quad \varphi_{n,\ell,m}(r,\theta,\varphi) = Y_{\ell,m}(\theta,\varphi)R_{n,\ell}(r)$$

eigenvalue equation for the radial wave function

$$\boxed{E_{n,\ell}R_{n,\ell}(r) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right)R_{n,\ell}(r)}$$

$$E = E_{kin} + E_{pot} = \frac{\vec{p}_r^{\,2}}{2m} + \frac{\vec{L}^2}{2mr^2} + E_{pot}$$

Schrödinger equation of the hydrogen atom 4 Comment 1

The equation underlined in red gives the Schrödinger equation with the angular momentum operator.

The orbital wave function $\varphi(\vec{r})$ can be decomposed into the spherical harmonic $Y_{\ell,m}$ and a radial function that only depends on r.

The equation outlined in red shows the eigenvalue equation for the radial wave function.

The angular momentum operator is replaced by its eigenvalues $\ell(\ell+1)\hbar^2$. The eigenvalue equation depends on the angular momentum quantum number ℓ. The radial wave function is additionally determined by a second quantum number n, which is called the main quantum number.

Schrödinger equation of the hydrogen atom 4 Comment 2

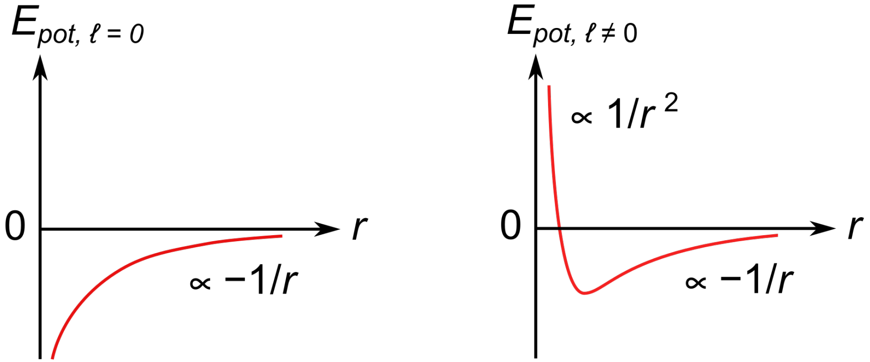
For comparison, the last equation shows the classical energy of a particle moving in a radial potential.

Each term of classical energy has its counterpart in the time-independent Schrödinger equation.

Schrödinger equation of the hydrogen atom 5

the effective potential energy

$$\boxed{E_{pot,\ell}(r) = \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$



Schrödinger equation of the hydrogen atom 5 Comment 1

The potential energy due to the Coulomb potential of the nucleus and the kinetic energy due to the angular momentum of the electron together form an effective potential energy.

When the angular momentum is zero, there is only the attractive force due to the nucleus, i.e. the proton in case of the hydrogen atom.

The electron can penetrate the nucleus without resistance.

In classical physics, the electron would perform an oscillating motion through the nucleus.

The energy oscillates between the radial kinetic energy of the electron and the potential energy due to the attractive force of the nucleus.

Schrödinger equation of the hydrogen atom 5 Comment 2

In classical physics, the electron would lose energy through the emission of electromagnetic radiation.

The Schrödinger equation shows that no electromagnetic radiation can be emitted due to this motion.

The probability density to find the electron results from the square of the wave function.

The wave function itself assumes a finite value for $r \to 0$ and the probability of finding the electron within the atomic nucleus is not zero.

Although the angular momentum is zero, application of the uncertainty principle shows that the particle cannot move in a straight line since the uncertainty of momentum perpendicular to the line of motion would be zero.

Schrödinger equation of the hydrogen atom 5 Comment 3

Since the spherical harmonic of an s orbital is a constant, all directions of motion are equally likely.

If the angular momentum of the electron is not equal to zero, the effective potential energy for $r \to 0$ becomes very large due to the angular momentum of the electron.

A strong repulsive force acts between the atomic nucleus and the electron, since the centrifugal force becomes very strong at small distances from the atomic nucleus.

The wave function of the electron becomes zero for $r \to 0$.

The probability of finding the electron in or near the nucleus is zero for electrons with angular momentum.

Schrödinger equation of the hydrogen atom 5 Comment 4

There is a big difference between so-called s-electrons and electrons with $\ell \neq 0$: s-electrons penetrate the nucleus, while electrons with angular momentum are kept away from the nucleus due to the centrifugal force.

This is why s-electrons are particularly sensitive to the properties of the nucleus.

Revision

Summary in Questions

1. Spherical harmonics are the eigenfunctions of the angular momentum operator. Explain the structure of the spherical harmonics.
2. Give the formulas of the spherical harmonics $Y_{1,-1}$, $Y_{1,0}$ and $Y_{1,+1}$ without the normalization factor.
3. Give the energy eigenvalues for the rotation of a diatomic molecule.
4. Show that cos θ is an eigenfunction of the angular momentum operators and determine the quantum number ℓ and m.