

Advanced Physical Chemistry (fizkemhk17em)

Electronic Structure

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Goal of this part of the course

- **Learn the English terms used in quantum chemistry**
 - „*Reminder*” section
- **Talk about topics left out the BSc course**
 - „*Angular momentum*” and „*Group Theory*” sections
- **Repetition with this new knowledge**
 - „*Atomic structure*” and „*Molecular structure*” sections
- **Learn the basic knowledge to perform quantum chemical calculations**
 - „*Methods*” section

Syllabus

See at <https://pgszalay.elte.hu/teaching>

- Last year's document: Advanced Physical Chemistry (Electronic Structure Part 2018)
- This year's document: will appear here in parts



Content of this part

- **Angular momentum:** operators, eigenvalues, eigenfunctions; magnetic moments; spin moments; application to the hydrogen atom.
- **Electronic structure of atoms:** orbitals, orbital energies, electronic configuration; angular momentum operators for many electron system; representation of atomic states and the corresponding notation; Hund's rule, spin-orbit interaction, atoms in magnetic field.
- **Molecular symmetry, group theory:** symmetry operations, point groups, representations and the character table, direct-product representation; application in electronic structure and spectroscopy.
- **Chemical bond:** quantum mechanical definition of chemical bond; approximations: IEA, MO theories, LCAO-MO, Valence Bond theory; diatomic molecules, electronic structure of transition-metal complexes; quantum chemistry of periodic systems.
- **Computational Chemistry:** determinant wave function, energy expression with determinant wave function, short derivation of the Hartree-Fock (HF) method, Hartree-Fock-Roothaan method, interpretation of the HF results (orbitals, density, population analysis, Koopmans theorem), basic elements of the Density Functional Theory (DFT), Hohenberg-Kohn theorems, Kohn-Sham DFT, functionals, hybrid methods; atomic basis sets.



Reminder

In quantum mechanics physical quantities are represented by operators.

Basic operators are the coordinate \hat{x} and momentum \hat{p} :

$$\begin{aligned}\hat{x} &= x \\ \hat{p} &= -i\hbar\frac{\partial}{\partial x}\end{aligned}$$

All other operators can be derived by replacing coordinate and momentum in the classical formula by the operators.

Example: kinetic energy

Reminder

Measurement

According to quantum mechanics, the result of a measurement can only be the eigenvalue of the corresponding operator.

$$\hat{A}\phi_i(x) = a_i\phi_i$$

where a_i is the i th eigenvalue, ϕ_i is corresponding eigenfunction.

Reminder

Two operators commute, if

$$\begin{aligned}\hat{A} \cdot \hat{B} - \hat{B} \cdot \hat{A} &= 0 \\ [\hat{A}, \hat{B}] &= 0\end{aligned}$$

i.e. their commutator is vanishing. In this case the corresponding two physical quantities can be measured simultaneously.

Otherwise, the two physical quantities can be measured only with some uncertainty:

$$\begin{aligned}[\hat{x}, \hat{p}_x] &= i\hbar \neq 0 \\ &\downarrow \\ \Delta x \cdot \Delta p_x &\geq \frac{1}{2}\hbar\end{aligned}$$

This is the famous *Heisenberg uncertainty principle*.



Angular momentum operators

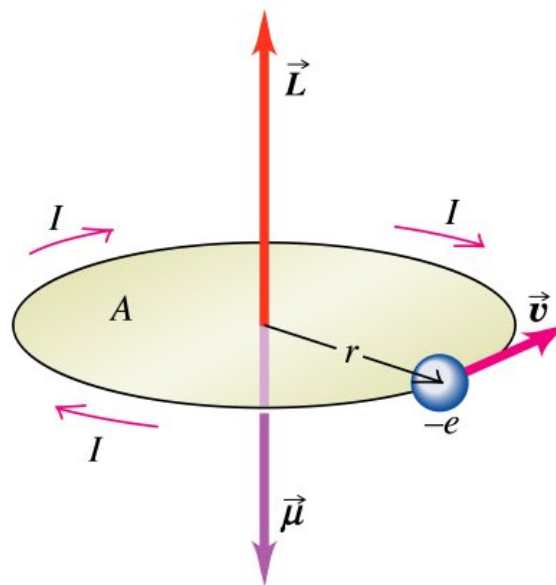
Classical angular momentum:

$$\underline{l} = \underline{r} \times \underline{p}$$

$$l_x = yp_z - zp_y$$

$$l_y = zp_x - xp_z$$

$$l_z = xp_y - yp_x.$$



Angular momentum operators

Classical angular momentum:

$$\underline{l} = \underline{r} \times \underline{p}$$

$$l_x = yp_z - zp_y$$

$$l_y = zp_x - xp_z$$

$$l_z = xp_y - yp_x.$$

Thus, with the definition of \hat{x} , and \hat{p} one can obtain the corresponding operators for the angular momentum:

$$\hat{l}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\hat{l}_y = \dots$$

$$\hat{l}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

$$\underline{\hat{l}}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$$

Angular momentum operators

It is easy to derive some important properties of the angular momentum operators:

$$\begin{aligned} [\hat{l}_x, \hat{l}_y] &= i\hbar \hat{l}_z \\ [\hat{l}_y, \hat{l}_z] &= i\hbar \hat{l}_x \\ [\hat{l}_z, \hat{l}_x] &= i\hbar \hat{l}_y \\ [\hat{l}^2, \hat{l}_i] &= 0, \quad i = x, y, z \end{aligned}$$

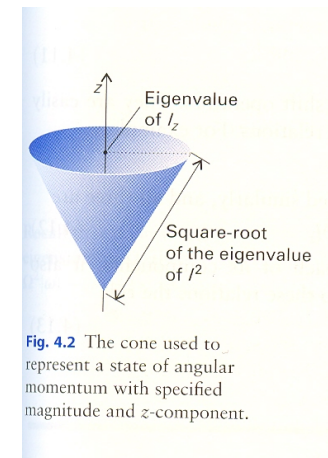


Fig. 4.2 The cone used to represent a state of angular momentum with specified magnitude and z-component.

This means that \hat{l} does not have any two components which can be measured at the same time. It is \hat{l}^2 (square length) and one component of \hat{l} which can be obtained simultaneously.

Angular momentum operators

z component of the angular momentum:

$$\hat{l}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Let us use a spherical coordinate system!

$$x = r \sin \vartheta \cos \varphi$$

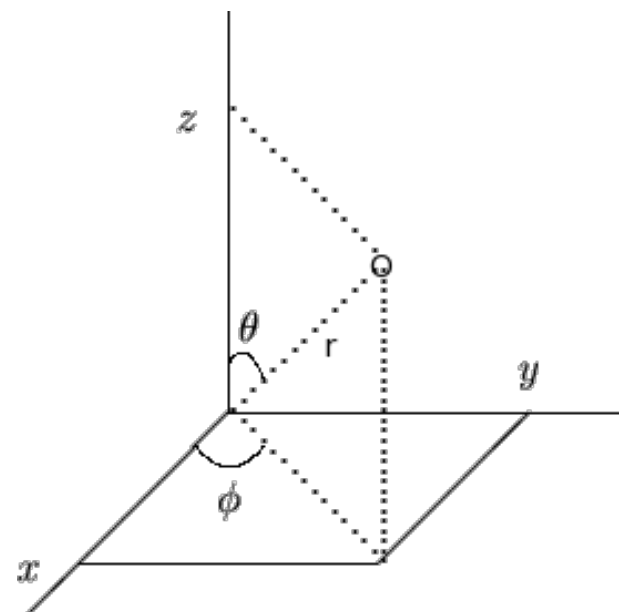
$$y = r \sin \vartheta \sin \varphi$$

$$z = r \cos \vartheta$$

$$\frac{\partial x}{\partial \varphi} = -r \sin \vartheta \sin \varphi = -y$$

$$\frac{\partial y}{\partial \varphi} = r \sin \vartheta \cos \varphi = x$$

$$\frac{\partial z}{\partial \varphi} = 0$$



Angular momentum operators

$$\frac{\partial x}{\partial \varphi} = -r \sin \vartheta \sin \varphi = -y$$

$$\frac{\partial y}{\partial \varphi} = r \sin \vartheta \cos \varphi = x$$

$$\frac{\partial z}{\partial \varphi} = 0$$

First we recognize that

$$\left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = \frac{\partial}{\partial \varphi}$$

One can easily prove this using the „chain-rule”:

$$\begin{aligned} \frac{\partial}{\partial \varphi} &= \frac{\partial}{\partial x} \frac{\partial x}{\partial \varphi} + \frac{\partial}{\partial y} \frac{\partial y}{\partial \varphi} + \frac{\partial}{\partial z} \frac{\partial z}{\partial \varphi} \\ &= -\frac{\partial}{\partial x} y + \frac{\partial}{\partial y} x + \frac{\partial}{\partial z} \cdot 0 = \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad QED \end{aligned}$$

Angular momentum operators

The z component of the angular momentum operator therefore reads:

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

Eigenfunctions and eigenvalues of the z component of the angular momentum:

$$l_z = m\hbar, \quad m = 0, \pm 1, \dots$$
$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} \cdot e^{im\varphi}, \quad m = 0, \pm 1, \dots$$

Angular momentum operators

\hat{l}^2 in spherical coordinates:

$$\hat{l}^2 = -\hbar^2 \left[\underbrace{\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right)}_{\hat{A}(\vartheta)} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right]$$

The eigensystem of the \hat{l}^2 operator

$$\lambda = l(l+1)\hbar^2 \quad l \geq |m|$$

$$Y_l^m(\vartheta, \varphi) = \Theta_l^m(\cos(\vartheta)) \cdot e^{im\varphi}$$

$$l = 0, 1, 2, \dots$$

$$m = -l, \dots, 0, \dots, l$$

Magnetic moment

If a charged particle is moving on a circle (has angular momentum), it also has magnetic moment. The magnetic moment vector ($\underline{\mu}$) is therefore proportional to the angular momentum vector, for example the z component is:

$$\hat{\mu}_z = \frac{e}{2 m_{el}} \hat{l}_z$$

The system having a magnetic moment will interact with the magnetic field, its energy will change due to this interaction:

$$\Delta E = B_z \cdot \frac{e}{2 m_{el}} \cdot l_z$$

where B_z is the z component of the *magnetic induction*, which is quantity characterizing the strength of the magnetic field.



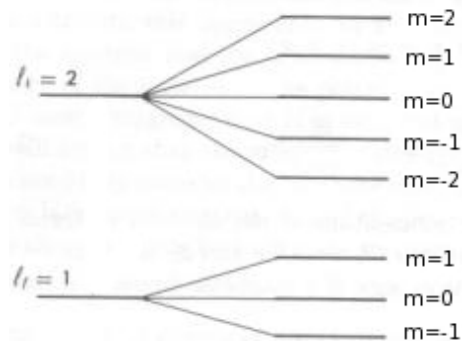
Magnetic moment

The possible values of $l_z = m \cdot \hbar$, where $m = 0, \pm 1, \dots$. Therefore

$$\Delta E = B_z \cdot \mu_B \cdot m$$

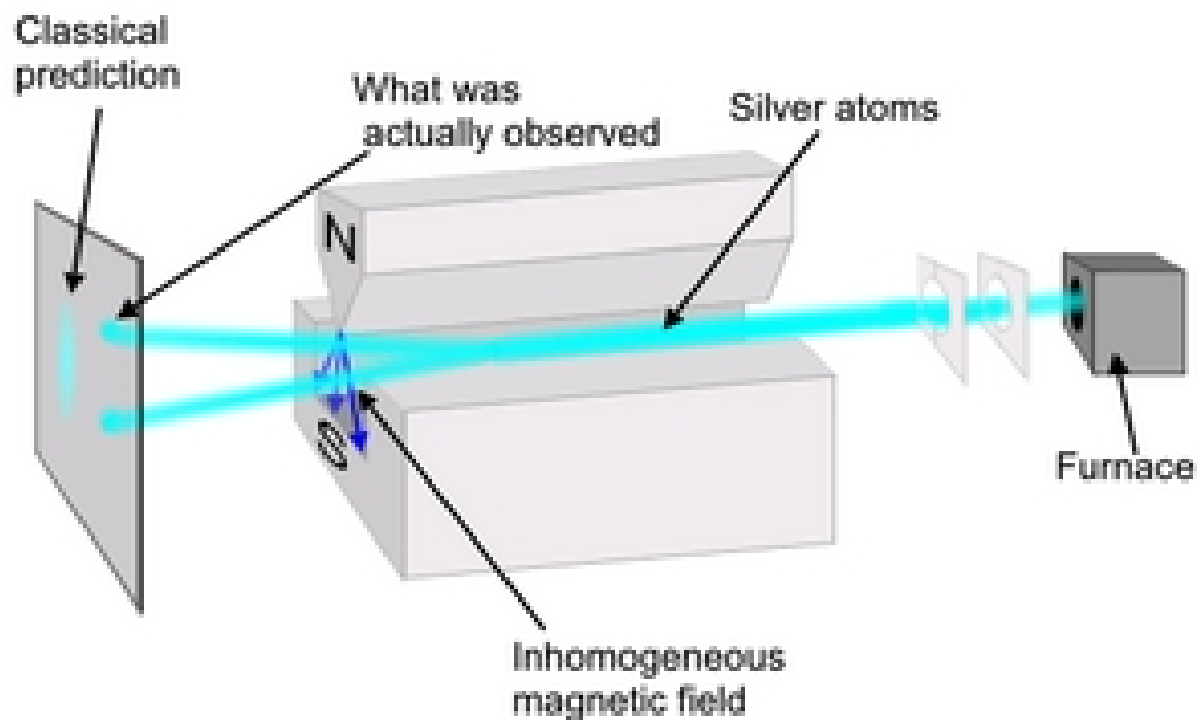
where $\mu_B = \frac{e\hbar}{2m_{el}}$ is a constant called *Bohr-magneton*.

What does this mean? According to the equations above, the energy of the particle with angular momentum in magnetic field depends on the quantum number m : if m is positive, it will grow; if m is negative, it will decrease; and it is not changing for $m = 0$. Since there are $2l + 1$ possible values of m , there will be $2l + 1$ different energy levels, the degeneracy of these levels will be lifted! This is the so called Zeeman-effekt.



The spin of the electron

Stern-Gerlach experiment:



The beam split into 2 beams, and not 1, 3, 5, 7, etc., as expected from the properties of the angular momentum!!

The spin of the electron

To explain this experiment

- Pauli (1925): a „fourth quantum number” is needed;
- Goudsmit and Uhlenbeck suggested the concept of *spin*, as the „internal angular momentum”

In mathematical form:

$$\underline{\hat{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$$

The spin of the electrons

The commutation properties of this new operator are the same as of the angular momentum, since it describes similar property:

$$[\hat{s}_x, \hat{s}_y] = i\hbar\hat{s}_z$$

$$[\hat{s}^2, \hat{s}_i] = 0 \quad i = x, y, z$$

Eigenvalues have again similar properties than in case of the angular momentum:

$$\hat{s}^2 \text{ eigenvalues : } s(s+1) [\hbar^2]$$

$$\hat{s}_z \text{ eigenvalues : } m_s = -s, -s+1, \dots, s [\hbar]$$

The spin of the electrons

What are the possible values of the new quantum numbers s and m_s ? This can be obtained from the Stern-Gerlach experiment: there were two beams, so that m_s can have only two values:

$$m_s = \frac{1}{2}, -\frac{1}{2}$$

Therefore

$$s = \frac{1}{2}$$

is the only proper choice!!!

Electron has a charge of -1 , and a spin of $\frac{1}{2}$!!!!

The spin of the electron

There are two eigenvalues of s_z , therefore there are two eigenfunctions $\alpha(\sigma)$ and $\beta(\sigma)$ (σ is the spin coordinate):

$$\hat{s}_z \alpha(\sigma) = \frac{1}{2} \alpha(\sigma)$$

$$\hat{s}_z \beta(\sigma) = -\frac{1}{2} \beta(\sigma)$$

Pauli matrices:

$$\hat{s}_z = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}$$

$$\hat{s}_x = \begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}$$

$$\hat{s}_y = \begin{pmatrix} 0 & -\frac{i}{2} \\ \frac{i}{2} & 0 \end{pmatrix}$$

The spin of the electron

The total wave function of the electron atom must be supplemented by the spin, thus it depends on four variables:

$$\Psi(x, y, z, \sigma) = u(x, y, z)\alpha(\sigma)$$

$$\text{or} = u(x, y, z)\beta(\sigma)$$

Spin-orbit interaction

There are two different types of angular momenta:

- angular momentum resulting from the motion of electrons ($\hat{\underline{l}}$), (*orbital angular momentum*);
- angular momentum originating from the spin ($\hat{\underline{s}}$) (*spin momentum*).

These magnetic moments can interact, causing an energy change:

$$\hat{H} \rightarrow \hat{H} + \zeta \cdot \hat{\underline{l}} \cdot \hat{\underline{s}}$$

where ζ is a constant.

Consequences:

- the Hamilton operator will not commute with \hat{l}^2 , \hat{l}_z and \hat{s}_z operators;
- energy will depend on the quantum number l .

Quantum mechanical description of the hydrogen atom

The Hamiltonian of the hydrogen atom (in atomic units):

$$\hat{H} = -\frac{1}{2}\Delta - \frac{1}{r}$$

The Hamiltonian in spherical coordinates:

$$\hat{H} = -\frac{1}{2} \left[\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(-\hat{l}^2 \right) \right] - \frac{1}{r}$$

Relation of the Hamiltonian with angular momentum:

$$\left[\hat{H}, \hat{l}_z \right] = 0 \quad \text{and} \quad \left[\hat{H}, \hat{l}^2 \right] = 0$$

Since \hat{l}_z and \hat{l}^2 depend only on the variables φ and ϑ , the wave function can be written as:

$$\Psi(r, \vartheta, \varphi) = R(r) Y_l^m(\vartheta, \varphi)$$

Quantum mechanical description of the hydrogen atom

Solution of the Schrödinger equation for the hydrogen atom

Eigenfunctions:

$$\Psi(r, \vartheta, \varphi) = R_{nl}(r) Y_l^m(\vartheta, \varphi) = R_{nl}(r) \Theta_l^m(\vartheta) e^{-im\varphi}$$

Eigenvalues (hartree units):

$$E_n = -\frac{1}{2n^2} (E_h)$$

Quantum numbers:

$$n = 1, 2, 3, \dots$$

$$l = 0, 1, 2, \dots, n - 1$$

$$m = -l, -l + 1, \dots, 0, l - 1, l$$

Quantum mechanical description of the hydrogen atom

Eigenfunctions of the hydrogen molecule (Ψ_{nlm}):

$$\begin{aligned}
 1s & \quad \Psi_{100} = \frac{1}{\sqrt{\pi}} e^{-r} \\
 2s & \quad \Psi_{200} = \frac{1}{4\sqrt{2\pi}} (2 - r) e^{-r/2} \\
 2p_0 & \quad \Psi_{210} = \frac{1}{4\sqrt{2\pi}} r e^{-r/2} \cos(\vartheta) \\
 2p_{\pm 1} & \quad \Psi_{21\pm 1} = \frac{1}{8\sqrt{\pi}} r e^{-r/2} \sin(\vartheta) e^{\pm i\varphi} \\
 3s & \quad \Psi_{300} = \frac{2}{81\sqrt{3\pi}} (27 - 18r + 2r^2) e^{-r/3} \\
 3p_0 & \quad \Psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} r (6 - r) e^{-r/3} \cos(\vartheta) \\
 3p_{\pm 1} & \quad \Psi_{31\pm 1} = \frac{1}{81\sqrt{\pi}} r (6 - r) e^{-r/3} \sin(\vartheta) e^{\pm i\varphi} \\
 3d_0 & \quad \Psi_{320} = \frac{1}{81\sqrt{6\pi}} r^2 e^{-r/3} (3 \cos^2(\vartheta) - 1) \\
 3d_{\pm 1} & \quad \Psi_{32\pm 1} = \frac{1}{81\sqrt{\pi}} r^2 e^{-r/3} \sin(\vartheta) \cos(\vartheta) e^{\pm i\varphi} \\
 3d_{\pm 2} & \quad \Psi_{32\pm 2} = \frac{1}{162\sqrt{\pi}} r^2 e^{-r/3} \sin^2(\vartheta) e^{\pm 2i\varphi}
 \end{aligned}$$

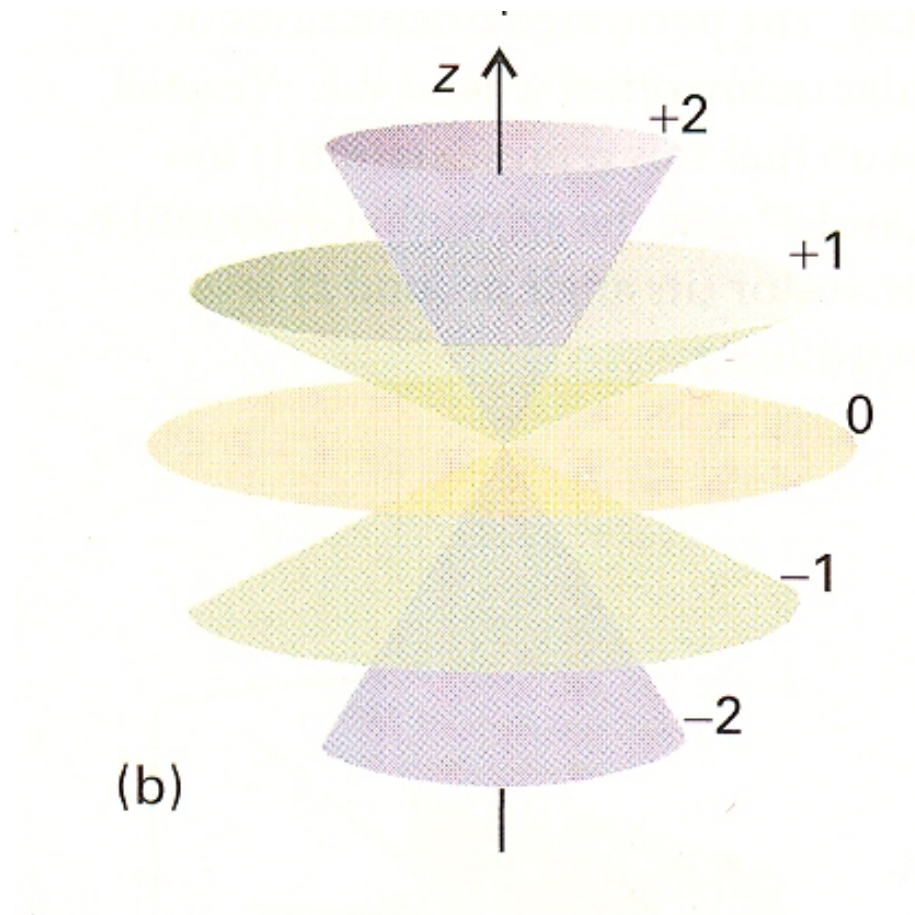
Angular momentum of the H atom

The angular momentum values belonging to the orbitals of the H atom:

orbital	n	l	m	$\lambda = l(l + 1)[\hbar^2]$	$l_z = m[\hbar]$
1s	1	0	0	0	0
2s	2	0	0	0	0
2p ₀	2	1	0	2	0
2p ₁	2	1	1	2	1
2p ₋₁	2	1	-1	2	-1
3s	3	0	0	0	0
3p ₀	3	1	0	2	0
3p ₁	3	1	1	2	1
3p ₋₁	3	1	-1	2	-1
3d ₀	3	2	0	6	0
3d ₁	3	2	1	6	1
3d ₋₁	3	2	-1	6	-1
3d ₂	3	2	2	6	2
3d ₋₂	3	2	-2	6	-2

Angular momentum of the H atom

Angular momentum vectors of the $3d$ orbitals:



The states of the hydrogen atom including spin

Wave function:

$$\Psi_{n,l,m,m_s}$$

Quantum numbers:

$$n = 1, 2, \dots$$

$$l = 0, 1, \dots, n - 1$$

$$m = -l, -l + 1, \dots, l$$

$$m_s = -\frac{1}{2}, \frac{1}{2}$$

Energy depends still only on quantum number n ($2n^2$ -fold degeneracy):

$$E_n = -\frac{1}{2n^2} [E_h]$$