

THE HYDROGEN ATOM : BASIS OF THE ATOMIC PHYSICS

All the chemistry can be theoretically built using the Schrödinger equation (Physicists point of view :))!
=> quantum chemistry

① The Schrödinger equation in 3 dimensions

We have discussed the Schrödinger equation and some of its applications for one dimensional problems. The straight line approach is adequate for some applications but to understand the atomic structure we need a 3D generalization. This 3D Schrödinger equation will be:

$$\boxed{-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x,y,z)}{\partial x^2} + \frac{\partial^2 \psi(x,y,z)}{\partial y^2} + \frac{\partial^2 \psi(x,y,z)}{\partial z^2} \right) + U(x,y,z) \psi(x,y,z) = i\hbar \frac{\partial \psi(x,y,z)}{\partial t}}$$

time dependent. eq.

Likewise 1D case:

$|\psi(x,y,z)|^2$ is the probability distribution in 3D function

The normalization condition in 3D is

$$\int_V |\psi(x,y,z)|^2 dV = 1$$

The time independent 3D Schrödinger eq will be:

$$\boxed{-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \phi(x,y,z)}{\partial x^2} + \frac{\partial^2 \phi(x,y,z)}{\partial y^2} + \frac{\partial^2 \phi(x,y,z)}{\partial z^2} \right) + U(x,y,z) \phi(x,y,z) = E \phi(x,y,z)}$$

with Obs 1 $\Psi(x,y,z) = \Phi(x,y,z) e^{-\frac{U\tau}{\hbar}}$

We introduce the Laplace operator:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

2nd order differential operator

Then, the 3D Schrödinger equation writes:

$$\left(-\frac{\hbar^2}{2m} \Delta + U(x,y,z) \right) \Psi(x,y,z) = E \Psi(x,y,z)$$

$$\hat{H} \Psi(x,y,z) = E \Psi(x,y,z)$$

\hat{H} = Hamilton operator (Hamiltonian) = total energy operator.

$$\hat{H} = \hat{K} + \hat{U}$$

\hat{K} = kinetic energy operator
 \hat{U} = potential energy operator

$$\begin{aligned} \hat{K} &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} = \\ &= \frac{\left(i\hbar \frac{\partial}{\partial x} \right)^2}{2m} + \frac{\left(i\hbar \frac{\partial}{\partial y} \right)^2}{2m} + \frac{\left(i\hbar \frac{\partial}{\partial z} \right)^2}{2m} = \\ &= \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{\hat{p}_z^2}{2m} \end{aligned}$$

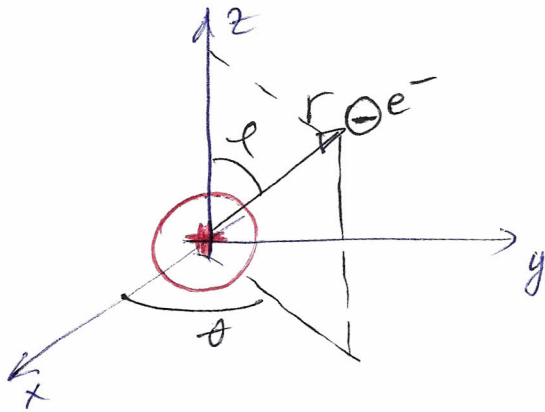
\Rightarrow momentum operators $\hat{p}_x = i\hbar \frac{\partial}{\partial x}$; $\hat{p}_y = i\hbar \frac{\partial}{\partial y}$
 $\hat{p}_z = i\hbar \frac{\partial}{\partial z}$

Obs 2 Each classical physical quantity have an equivalent quantum operator (one of the postulates of the quantum mechanics (in the advanced Dirac formulation)).

② The hydrogen atom

- 3 -

The potential energy of the electron moving around the nucleus is spherically symmetric, it depends only on the distance $r = \sqrt{x^2 + y^2 + z^2}$



$$\begin{cases} x = r \cos \theta \sin \varphi \\ y = r \sin \theta \sin \varphi \\ z = r \cos \theta \end{cases}$$

$$U(\vec{r}) = \frac{e^2}{4\pi\epsilon_0 r}$$

The time independent Schrödinger equation:

$$\left(-\frac{\hbar^2}{2m} \Delta + U(\vec{r}) \right) \phi(\vec{r}) = E \phi(\vec{r})$$

Because of the spherical symmetry of $U(\vec{r})$ it is worthful to solve this equation in spherical coordinates.

The $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ Laplace operator in

spherical coordinates writes as:

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

The mathematical solutions of this equations can be written as a product between a RADIAL FUNCTION $R_{nl}(r)$ and an orbital function $Y_l^m(\theta, \varphi)$ called in math spherical harmonics

$$\Phi_{nlm}(\theta, \varphi) = R_{nl}(r) Y_l^m(\theta, \varphi)$$

The analytical solution is complicated and long and gets beyond the purpose of this course. However, what we should remark is that the wave function depends on three numbers n, l, m called quantum numbers. (their origin comes from the boundary conditions for the functions $R(r), Y_l^m(\theta, \phi)$)

n is the principal quantum number and it corresponds to the K, L, M, N, ... shells and quantifies the total energy of the electron in the atom:

$$E_n = - \frac{1}{(4\pi\epsilon_0)^2} \frac{me^4}{2n^2\hbar^2} = - \frac{13,6 \text{ eV}}{n^2}$$

identical to the one found in the Bohr's model.

\Rightarrow Schrödinger and Bohr approaches give similar energy levels scheme.

l = orbital (angular-momentum) quantum number

which implicates discrete (quantified) values of the orbital momentum L of the electron

$$L = \sqrt{l(l+1)} \hbar \quad l = 0, 1, 2, \dots, n-1$$

orbital quantum number

l	0	1	2	3	4	5
state	s	p	d	f	g	h

\rightarrow SPECTROSCOPIC NOTATION

m_l = magnetic quantum number $m_l \in [-l, l]$

ex

$l=1$	$m_l = -1, 0, 1$
$l=2$	$m_l = -2, -1, 0, 1, 2$

We quantize the possible values of component of \vec{L} in a given direction:

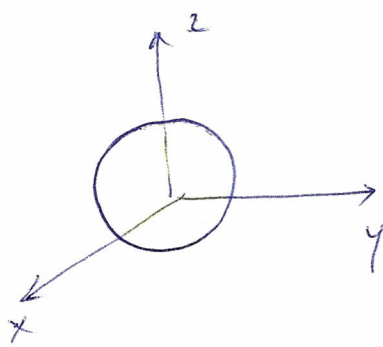
e.g. $L_z = m_l \hbar$

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

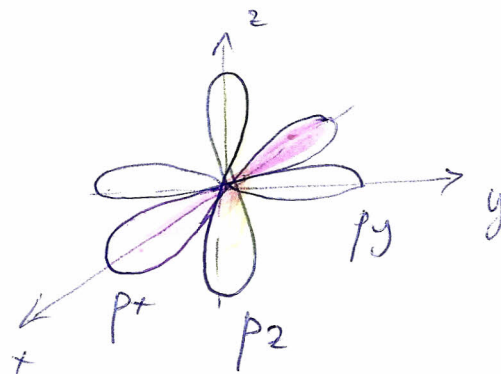
Electron probability distributions, Orbitals

The three dimensional probability distribution function $|\psi|^2$ for the different hydrogen wave functions (\Rightarrow) atomic orbitals

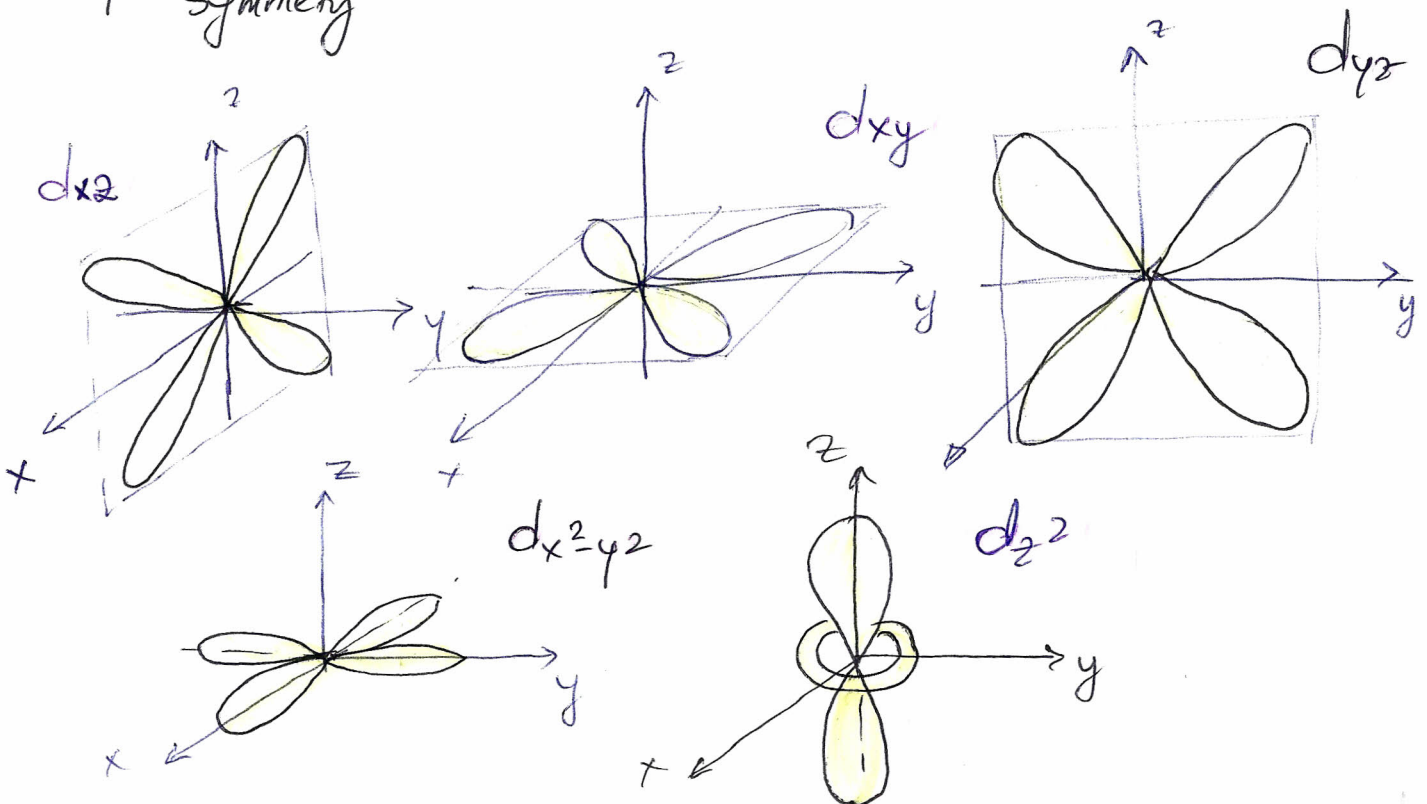
Obs: $e|\psi|^2 = \rho(r, \theta, \phi)$ = electronic charge density distribution



1s orbital
Spherical symmetry

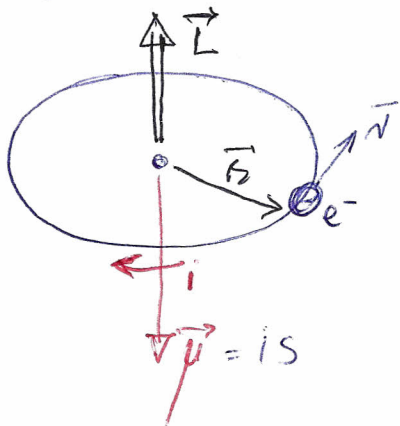


2p orbitals



Electron spin

Recall that an orbiting electron generates a microscopic magnetic moment:



$$\Rightarrow \vec{\mu} = \frac{e}{2m} \vec{L}$$

The potential energy of the interaction between $\vec{\mu}$ and an external field \vec{B}

is
$$U = -\vec{\mu} \cdot \vec{B}$$

Suppose that \vec{B} is along the z axis \Rightarrow

$$U = -\mu_z B \quad \text{but } \mu_z = \frac{e}{2m} L_z$$

$$L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

$$\Rightarrow \mu_z = m_l \frac{e \hbar}{2m} = m_l \mu_B$$

$\mu_B = \frac{e \hbar}{2m}$
Bohr magneton

\Rightarrow
$$U = -m_l \mu_B B$$
 orbital magnetic interaction energy

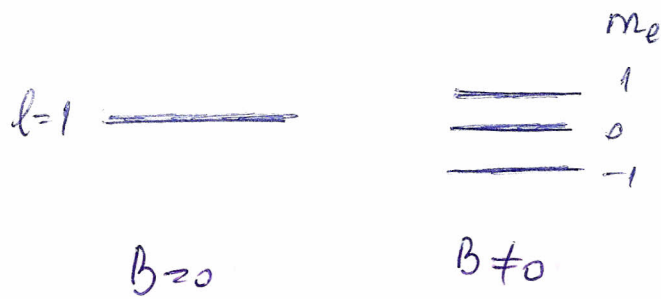
\Rightarrow The magnetic field shifts the energy of each orbital state by an amount U \Rightarrow

In external magnetic field an energy level with a particular ~~level~~ quantum number l contains $(2l+1)$ different orbital states. Without magnetic field these states have the same energy; that is they are degenerate

In the presence of \vec{B} they are split into $(2l+1)$ distinct energy levels spaced by $\mu_B B$.

This is called Zeeman-splitting

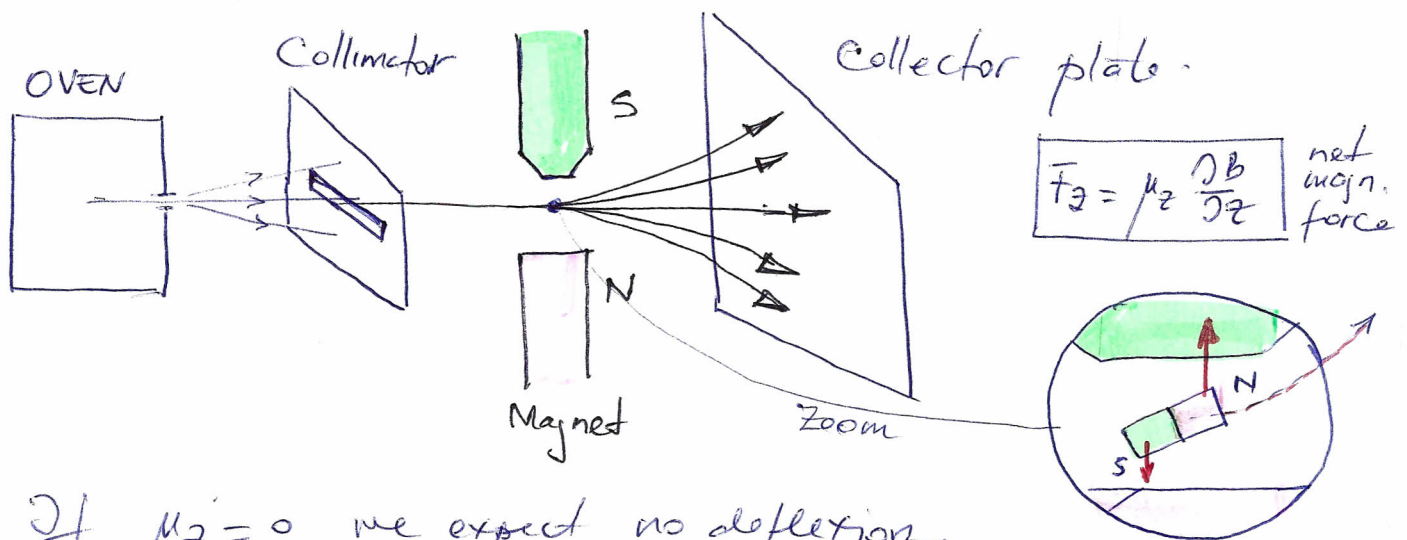
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$l=0$ no splitting, because no magnetic moment

Stern and Gerlach experiment

Otto Stern & Walter Gerlach developed an experiment to measure the magnetic moments of atoms. Their apparatus (fig) prepare an atomic beam by evaporating atoms out of a hole in an "oven". These atoms, travelling in a vacuum, pass through a non-uniform magnetic field* which can exert a net force on magnetic moments. So that moments μ_z tilted upward are deflected upward and μ_z tilted downward are deflected downward by the field.

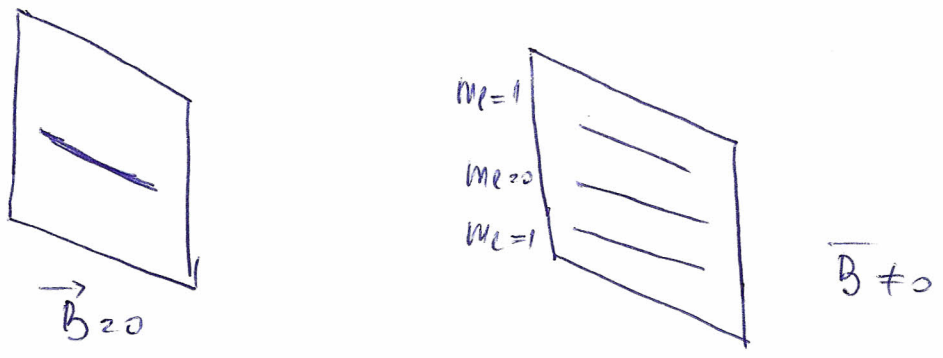


If $\mu_z = 0$ we expect no deflection.

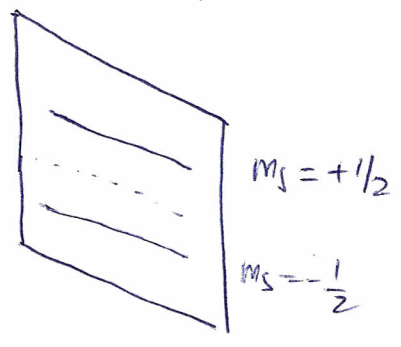
* the non-uniform \vec{B} is produced by the different shape of the S pole \Rightarrow force exerted by S pole $>$ force exerted by N pole \Rightarrow NET FORCE

Because the deflection depends on $\mu_z = -\frac{e}{2m} L_z$
 \Rightarrow by measuring μ_z one can determine L_z of the atoms in the atomic beam.

Ok When B is turned off, the beam is no-more splitted and deflected.



In 1927, with Schrödinger quantum theory developed, the Stern-Gerlach technique was used to measure the magnetic moment of hydrogen atoms. The ground state of H is $1s$, with $l=0$, so the atoms have no magnetic moment and there should be no deflection at all. However, the experiment produced two peaked distributions



An explanation for this was suggested, then confirmed: the electron has an inherent magnetic moment called SPIN. MAGNETIC MOMENT $\vec{\mu}_s$ \Leftrightarrow built-in magnetic moment

- \Rightarrow electron
 - intrinsic charge $-e = -1.6 \cdot 10^{-19} C$
 - mass: $m_e = 9.1 \cdot 10^{-31} kg$
 - Spin magnetic moment μ_s

- 10 -

If the electron has an inherent magnetic moment, it must have an inherent (intrinsic) angular momentum. This is called SPIN \vec{S} .

Obs. Classically, the spin is often associated with the spinning around own axis. However, quantum mechanically this is not true because the electron is an elementary particle, dimensionless (point particle) for which the rotation makes no sense.

The outcome of the Stern-Gerlach experiment tells us that the z component of this spin angular momentum is:

$$S_z = m_s \hbar \quad \text{where} \quad m_s = +\frac{1}{2}, -\frac{1}{2}$$

$m_s =$ spin quantum number

The $m_s = \frac{1}{2}$ state with $S_z = +\frac{1}{2} \hbar$ is called \uparrow
SPIN-UP STATE

$m_s = -\frac{1}{2}$ state with $S_z = -\frac{1}{2} \hbar$ is called \downarrow
SPIN-DOWN STATE

Analogous to L , the spin angular momentum

$$S = \sqrt{s(s+1)} \hbar \quad \text{where} \quad s = \frac{1}{2}$$

Obs: ① The stationary states of an atom are entirely described by four quantum numbers:
(n, l, m, m_s).

The spin orientation does not affect atom's energy so, a ground state electron in hydrogen can be in either $(1, 0, 0, +1/2)$ up state or $(1, 0, 0, -1/2)$ down state.

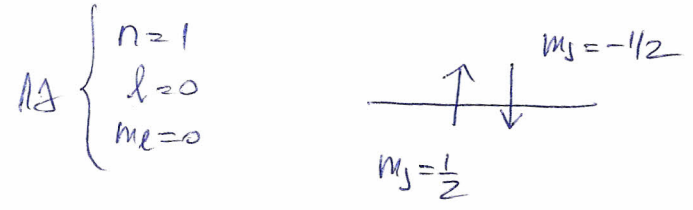
② The fact that $S = \frac{1}{2}$ has a single value has an interesting consequence. The corresponding principle tells us that a quantum particle starts to "act classical" in the limit of large quantum numbers. But S cannot become large \Rightarrow The electron's spin is an intrinsic quantum property of the electron and has no classical counterpart.

* The Schrödinger eq. can be solved in case of atoms with more electrons similarly, The i electron has $U_i = -\frac{Ze^2}{4\pi\epsilon_0 r_i} + U_{elec}(r_i)$
 \Rightarrow Multielectron atoms. Pauli exclusion principle

1925 Wolfgang Pauli

On the same quantum state we cannot put two electrons with the same set of quantum numbers (n, l, m_l, m_s) .

e.g. on an s state ($l=0$) we can put maximum 2 electrons with different spin.



In this way, one can establish the electronic configuration of atoms \Rightarrow periodic table of elements.

