

# Chemistry 3P51 – Fall 2013

## Quantum Chemistry

Lecture No. 24  
Nov 4<sup>th</sup>, 2013

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### *Objectives*

- To recall the main concepts of orbital angular momentum of hydrogenic atoms.
- To summarize the quantum numbers of hydrogenic systems.
- To introduce the concept of electron spin motivated by the Stern-Gerlach experiment.
- To introduce the spin angular momentum operator as well as its eigenfunctions and eigenvalues.
- To introduce spin functions and spin-orbitals.

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## Orbital angular momentum in hydrogenic atoms

The “orbital motion” of the electron in a hydrogenic atom is associated with an angular momentum, which is represented by the operator

$$\hat{\mathbf{L}} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$$

Recall that the wave functions for the hydrogenic atom are

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

where  $Y_l^m(\theta, \varphi)$  are spherical harmonics. The spherical harmonics are eigenfunctions of the angular momentum operators

$$\hat{L}^2 Y_l^m(\theta, \varphi) = \hbar^2 l(l+1) Y_l^m(\theta, \varphi)$$

$$\hat{L}_z Y_l^m(\theta, \varphi) = \hbar m Y_l^m(\theta, \varphi)$$

Therefore, the hydrogenic atom orbitals are also eigenfunctions of the angular momentum operators  $\hat{L}^2$  and  $\hat{L}_z$  with the same eigenvalues as the corresponding spherical harmonics.

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## Quantum numbers of the H-atom wave-function

$n$  The **principal quantum number** specifies the energy of the hydrogen atom

$$E_{nlm} = -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{2n^2} \quad n = 1, 2, 3, \dots$$

$l$  The **angular momentum quantum number** (also called the azimuthal quantum number) specifies the magnitude of the orbital angular momentum of the electron

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

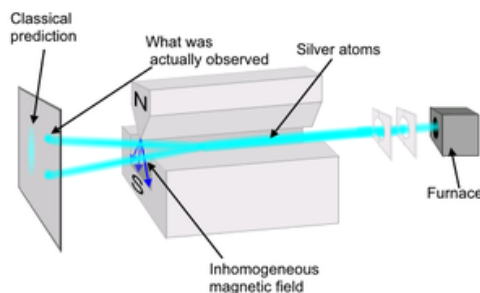
$m$  The so-called **magnetic quantum number** specifies the magnitude of the  $z$ -component of the angular momentum

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

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## Electron spin

Stern and Gerlach (1921) discovered that a beam of Ag atoms ( $[\text{Kr}]4d^{10}5s^1$ ,  $l = 0$ ) is split into two by an inhomogeneous magnetic field.



Schematic representation of the Stern-Gerlach experiment. Each Ag atom has one unpaired electron.

To explain this effect, Godsmit and Uhlenbeck (1925) put forward a hypothesis that an electron has its own (intrinsic) angular momentum  $\mathbf{S}$ , in addition to the orbital angular momentum  $\mathbf{L}$ .

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## Spin angular momentum

We designate the spin angular momentum by the vector  $\mathbf{S}$ , just as we use  $\mathbf{L}$  to represent the orbital angular momentum.

The spin angular momentum behaves in most ways like other angular momenta. In particular, its magnitude and direction are quantized. The magnitude of  $\mathbf{S}$  for a single electron is given by

$$S = \hbar \sqrt{s(s+1)}$$

where  $s$  is a *quantum number* which is called **spin**.

For an electron, *spin* always has the *half-integer* value

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

Thus, the magnitude of the spin angular momentum for a single electron is

$$S = \hbar \sqrt{s(s+1)} = \hbar \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \frac{\sqrt{3}}{2} \hbar$$

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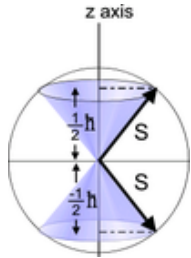
## Components of the spin angular momentum

Components of the spin angular momentum are analogous to those of the orbital angular momentum in that only one component is a constant of motion, characterized by a quantum number. As usual, this component is chosen to be  $S_z$ , and its value is given by

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

The quantum number  $m_s$  is called the **spin quantum number**

This means that the  $z$ -component of the spin angular momentum is quantized and can assume only two particular values:



$$S_z = \pm \frac{1}{2} \hbar$$

The case  $m_s = +\frac{1}{2}$  is referred to as “spin-up”, and  $m_s = -\frac{1}{2}$  is referred to as “spin-down”.

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## Spin functions

The spin angular momentum and its  $z$  component are represented by the quantum-mechanical operators  $\hat{S}^2$  and  $\hat{S}_z$  which are comparable with the operators  $\hat{L}^2$  and  $\hat{L}_z$

The operators  $\hat{S}^2$  and  $\hat{S}_z$  commute and, hence, share a common set of eigenfunctions. The eigenfunctions of these operators are called **spin eigenfunctions** and are represented by  $\alpha$  and  $\beta$ :

$$\hat{S}^2 \alpha = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \alpha = \frac{3}{4} \hbar^2 \alpha$$

$$\hat{S}^2 \beta = \frac{1}{2} \left( \frac{1}{2} + 1 \right) \hbar^2 \beta = \frac{3}{4} \hbar^2 \beta$$

$$\hat{S}_z \alpha = \frac{1}{2} \hbar \alpha$$

$$\hat{S}_z \beta = -\frac{1}{2} \hbar \beta$$

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## Spin-orbitals

The spin eigenfunctions  $\alpha$  and  $\beta$  do not involve spatial coordinates. Instead, they are functions of a formal “spin variable”  $\sigma$ .

The spin eigenfunctions  $\alpha$  and  $\beta$  are orthonormal:

$$\int \alpha^* \alpha d\sigma = \int \beta^* \beta d\sigma = 1$$

$$\int \alpha^* \beta d\sigma = \int \beta^* \alpha d\sigma = 0$$

A complete wavefunction for a hydrogenic atom must indicate the spin state of the electron. Since there are two spin functions, there are twice as many wavefunctions for the hydrogen atom as we indicated earlier:

$\psi_{nlm}\alpha$  and  $\psi_{nlm}\beta$  for each of the previous  $\psi_{nlm}$  's

The complete wavefunctions such as  $\psi\alpha$  and  $\psi\beta$  are called **spin-orbitals**.

A complete state specification for the electron in a hydrogenic atom requires the four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .

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## Degeneracies of the hydrogenic atom energy levels

