

# SCHRODINGER EQUATION FOR HYDROGEN

The Schrodinger Equation for hydrogen is written using the 3-dimensional spherical polar coordinate system version of the equation with the Coulomb potential  $-k_e e^2/r$  used for the potential energy operator. The reduced mass  $\mu = m_p m_e / (m_p + m_e)$  is used to include the kinetic energy contribution from both electron and proton.

$$\hat{K}\Psi + \hat{U}\Psi = E\Psi \Rightarrow -(\hbar^2/2\mu)\nabla^2\Psi(r,\theta,\varphi) - (k_e e^2/r)\Psi(r,\theta,\varphi) = E\Psi(r,\theta,\varphi)$$

$$(-\hbar^2/2\mu)[\Psi_{rr} + 2r^{-1}\Psi_r + r^{-2}\Psi_{\theta\theta} + r^{-2}\cot\theta\Psi_\theta + r^{-2}\csc^2\theta\Psi_{\varphi\varphi}] - (k_e e^2/r)\Psi = E\Psi$$

How this Schrodinger Equation is solved: Assume that the solution can be written as the product of radial, polar, and azimuthal functions:  $\Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$ . Substitute this expression into the Schrodinger and three ordinary differential equations result, coupled by three quantum numbers ( $n$ ,  $\ell$ , and  $m_\ell$ ). Solve these equations and obtain  $R(r)$ ,  $\Theta(\theta)$ , and  $\Phi(\varphi)$ . Construct the full solution as  $\Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$ .

# WAVE FUNCTIONS OF HYDROGEN

Below is the general form of the normalized wave function solutions to the Schrodinger equation for hydrogen in spherical polar coordinates. The functions  $L(2r/na)$  below are associated Laguerre polynomials, and the functions  $Y(\cos\theta, \varphi)$  are spherical harmonics. Examples of these types of functions are shown on the next frame.

$$\Psi_{n\ell m_\ell}(r, \theta, \varphi) = \left[ \frac{4(2\ell + 1)(n - \ell - 1)!}{\pi n^4 a^3 (n + \ell)!} \right]^{1/2} (2r/na)^\ell e^{-r/na} L(2r/na) Y_\ell^m(\theta, \varphi)$$

The constant  $a$  is the (first) Bohr radius  $a = .0529 \text{ nm}$

The index  $n$  is the principal quantum number:  $n = 1, 2, 3, \dots$

The index  $\ell$  is the orbital quantum number:  $\ell = 0, 1, 2, \dots, n-1$

The index  $m_\ell$  is the orbital magnetic quantum number:  $m_\ell = -\ell, \dots, +\ell$

# WAVE FUNCTIONS AND ENERGIES

Below are wave functions associated with a few of the lowest ( $n < 4$ ) energy states of the hydrogen atom (electron spin not considered). The energies (eigenvalues) associated are indicated as well. Note:  $E_{n\ell m_\ell} = -(13.6 \text{ eV})/n^2$ .

$$\Psi_{100} = (1/\pi a^3)^{1/2} e^{-r/a}$$

$$E_{100} = -13.6 \text{ eV}$$

$$\Psi_{200} = (1/32\pi a^3)^{1/2} (2 - r/a) e^{-r/2a}$$

$$E_{200} = -3.40 \text{ eV}$$

$$\Psi_{210} = (1/32\pi a^3)^{1/2} (r/a) e^{-r/2a} \cos\theta$$

$$E_{210} = -3.40 \text{ eV}$$

$$\Psi_{21\pm 1} = (1/64\pi a^3)^{1/2} (r/a) e^{-r/2a} \sin\theta e^{\pm i\phi}$$

$$E_{21\pm 1} = -3.40 \text{ eV}$$

$$\Psi_{300} = (1/19683\pi a^3)^{1/2} (27 - 18r/a + 2r^2/a^2) e^{-r/3a}$$

$$E_{300} = -1.51 \text{ eV}$$

$$\Psi_{310} = (2/6561\pi a^3)^{1/2} (r/a) (6 - r/a) e^{-r/3a} \cos\theta$$

$$E_{310} = -1.51 \text{ eV}$$

$$\Psi_{31\pm 1} = (1/6561\pi a^3)^{1/2} (r/a) (6 - r/a) e^{-r/3a} \sin\theta e^{\pm i\phi}$$

$$E_{31\pm 1} = -1.51 \text{ eV}$$

$$\Psi_{320} = (1/39366\pi a^3)^{1/2} (r/a)^2 e^{-r/3a} (3\cos^2\theta - 1)$$

$$E_{320} = -1.51 \text{ eV}$$

$$\Psi_{32\pm 1} = (1/6561\pi a^3)^{1/2} (r/a)^2 e^{-r/3a} \sin\theta \cos\theta e^{\pm i\phi}$$

$$E_{32\pm 1} = -1.51 \text{ eV}$$

$$\Psi_{32\pm 2} = (1/26244\pi a^3)^{1/2} (r/a)^2 e^{-r/3a} \sin^2\theta e^{\pm i2\phi}$$

$$E_{32\pm 2} = -1.51 \text{ eV}$$

# HYDROGEN PROBABILITY DENSITIES

Below are the probability density functions associated with a few of the lowest energy states ( $n < 4$ ) of the hydrogen atom (electron spin not considered). These functions are  $|\Psi_{n\ell m_\ell}|^2$  or  $\Psi_{n\ell m_\ell}^* \Psi_{n\ell m_\ell}$ .

$$|\Psi_{100}|^2 = (1/\pi a^3)e^{-2r/a}$$

$$|\Psi_{200}|^2 = (1/32\pi a^3)(2 - r/a)^2 e^{-r/a}$$

$$|\Psi_{210}|^2 = (1/32\pi a^3)(r/a)^2 e^{-r/a} \cos^2\theta$$

$$|\Psi_{21\pm 1}|^2 = (1/64\pi a^3)(r/a)^2 e^{-r/a} \sin^2\theta$$

$$|\Psi_{300}|^2 = (1/19683\pi a^3)(27 - 18r/a + 2r^2/a^2)^2 e^{-2r/3a}$$

$$|\Psi_{310}|^2 = (2/6561\pi a^3)(r/a)^2 (6 - r/a)^2 e^{-2r/3a} \cos^2\theta$$

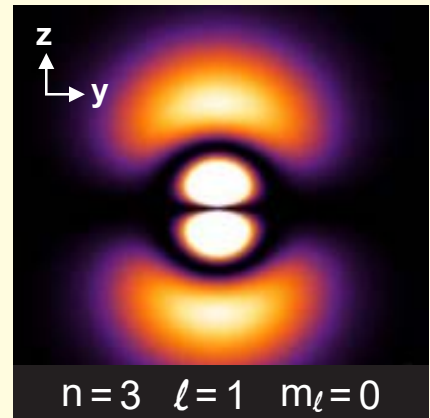
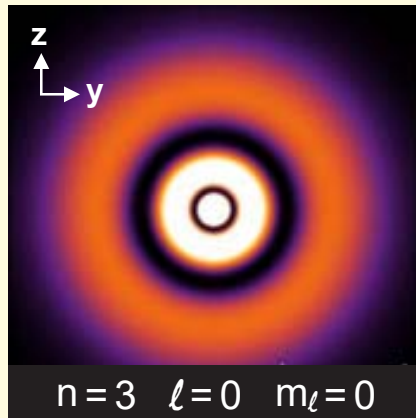
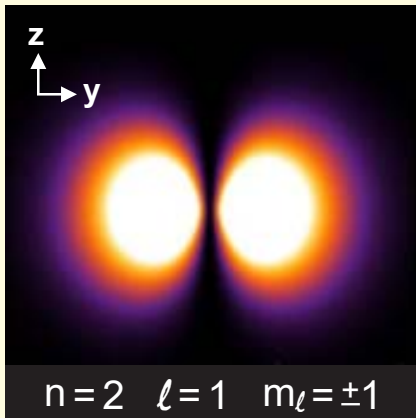
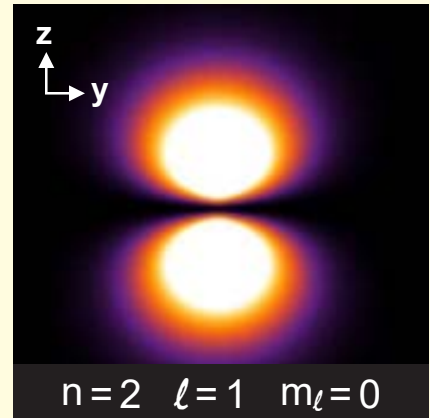
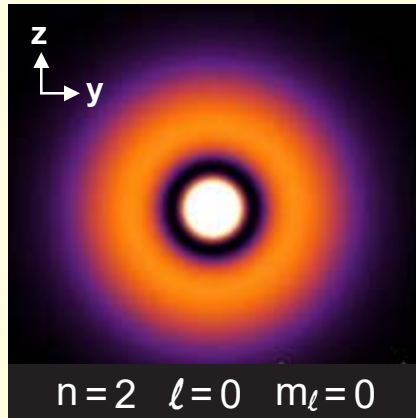
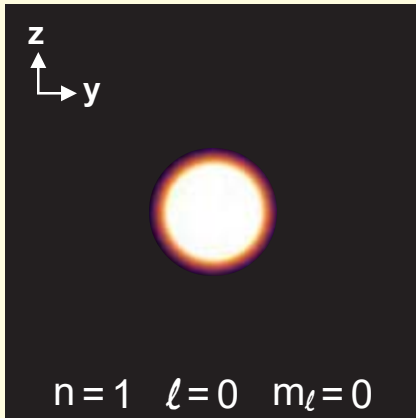
$$|\Psi_{31\pm 1}|^2 = (1/6561\pi a^3)(r/a)^2 (6 - r/a)^2 e^{-2r/3a} \sin^2\theta$$

$$|\Psi_{320}|^2 = (1/39366\pi a^3)(r/a)^4 e^{-2r/3a} (3\cos^2\theta - 1)^2$$

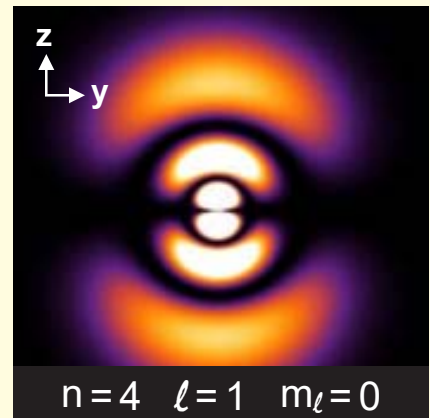
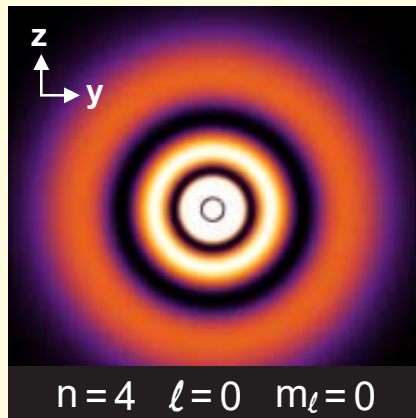
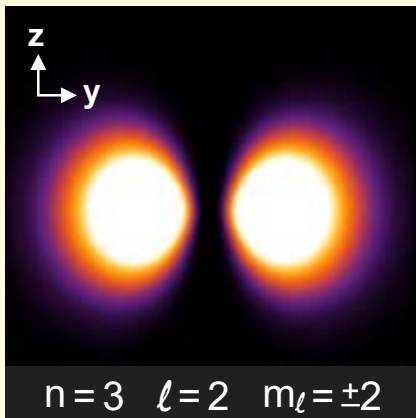
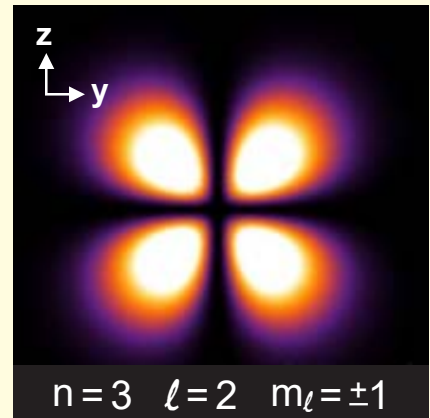
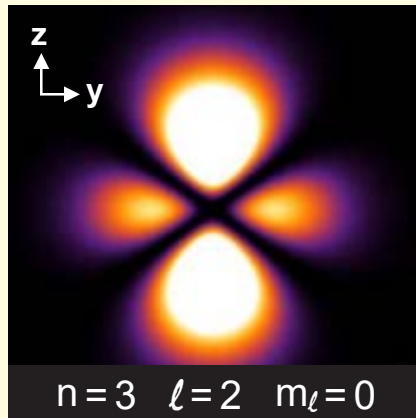
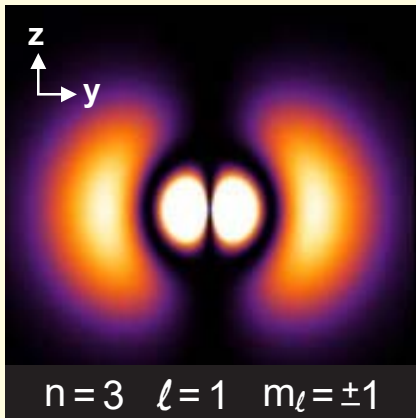
$$|\Psi_{32\pm 1}|^2 = (1/6561\pi a^3)(r/a)^4 e^{-2r/3a} \sin^2\theta \cos^2\theta$$

$$|\Psi_{32\pm 2}|^2 = (1/26244\pi a^3)(r/a)^4 e^{-2r/3a} \sin^4\theta$$

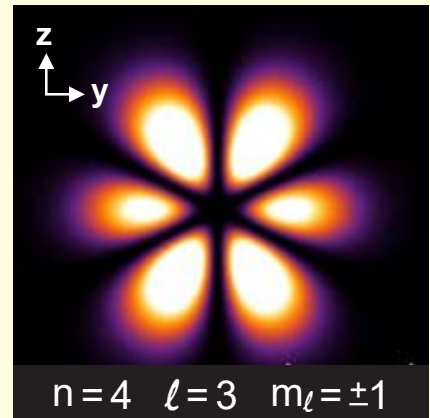
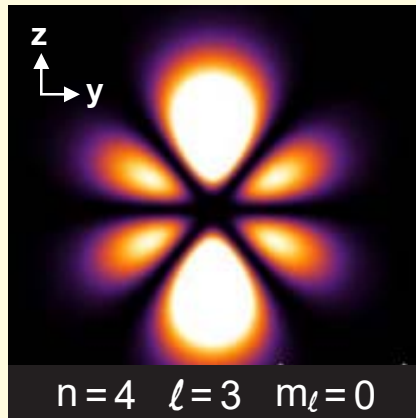
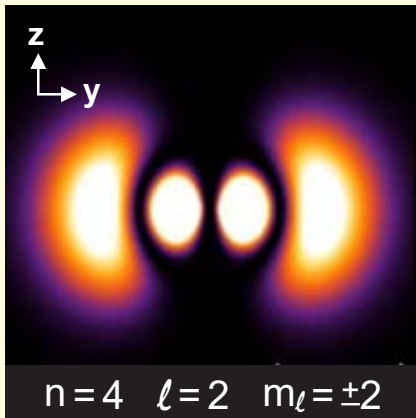
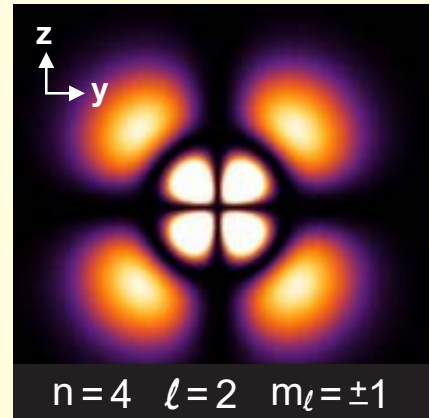
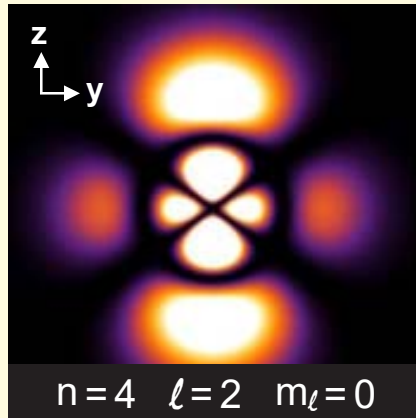
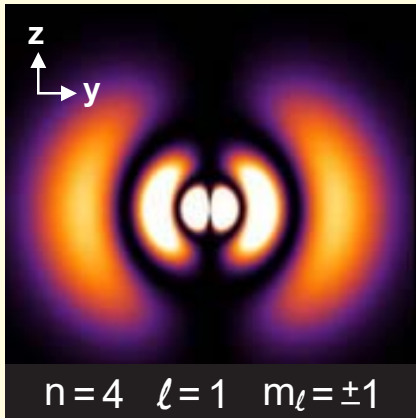
# HYDROGEN PROBABILITY DENSITIES $|\Psi_{n\ell m_\ell}|^2$



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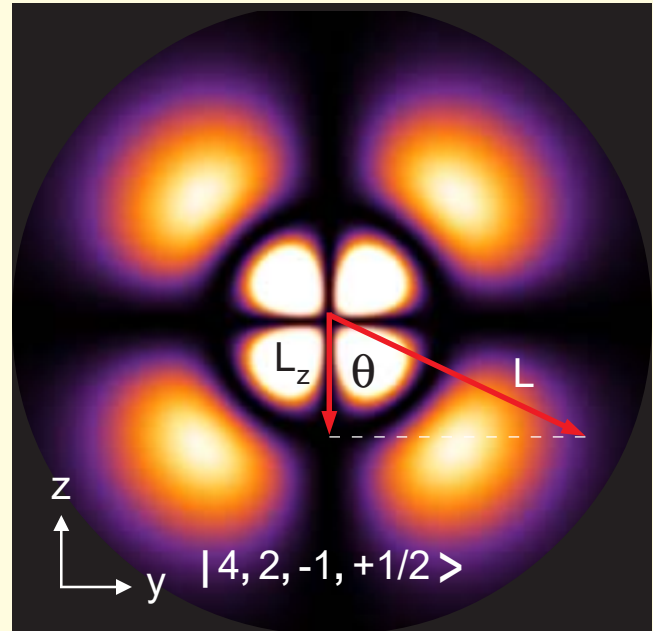


# HYDROGEN PROBABILITY DENSITIES $|\Psi_{n\ell m_\ell}|^2$



# PRINCIPAL QUANTUM NUMBER

The **principal quantum number  $n$**  ( $n = 1, 2, 3, \dots$ ) is understood as an index of the radial extent of the wave function. The larger  $n$  is, the greater the expectation value  $\langle r \rangle$  of the electron's distance from the proton. The principal quantum number  $n$  also determines the total energy of the atom, as the energy of the hydrogen atom in any quantum state is given by  $E_{n\ell m_\ell} = -(13.6 \text{ eV})/n^2$ . There are  $n - 1$  radial nodes in the wave function of a hydrogen atom.

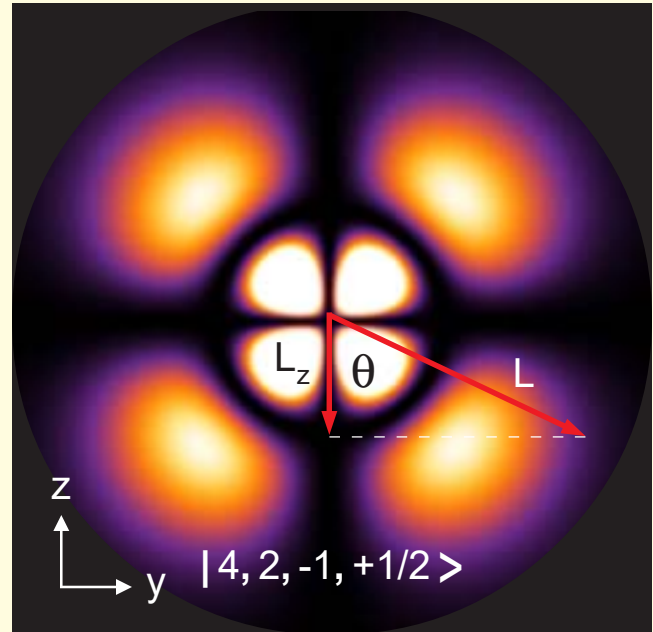




# ORBITAL QUANTUM NUMBER

The **orbital quantum number  $\ell$**  ( $\ell = 0, 1, 2, \dots, n-1$ ) is understood as an index of the orbital angular momentum the hydrogen atom has in a quantum state. The magnitude of the orbital angular momentum  $L$  of a hydrogen atom in the quantum state  $|n, \ell, m_\ell, m_s\rangle$  is  $L = [\ell(\ell + 1)]^{1/2} \hbar$  (J·s).

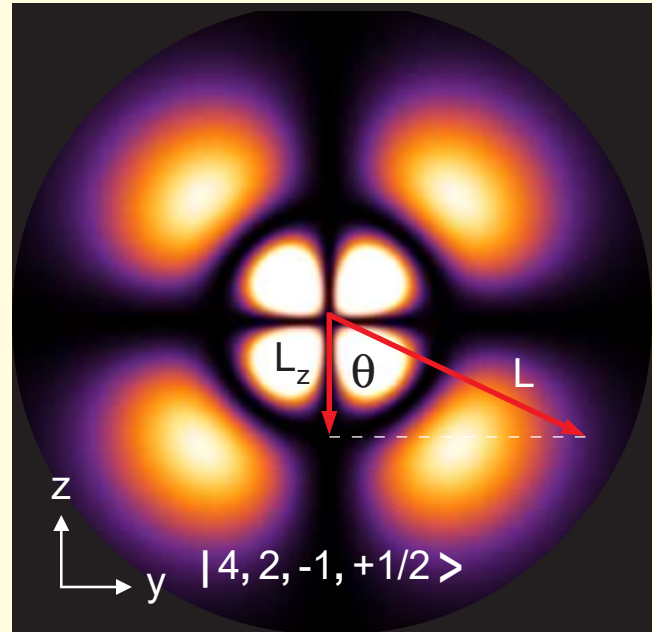
**example:** For the quantum state shown in the figure to the right,  $L = [2(2 + 1)]^{1/2} \hbar = 2.449 \hbar$ .



# ORBITAL MAGNETIC QUANTUM NUMBER

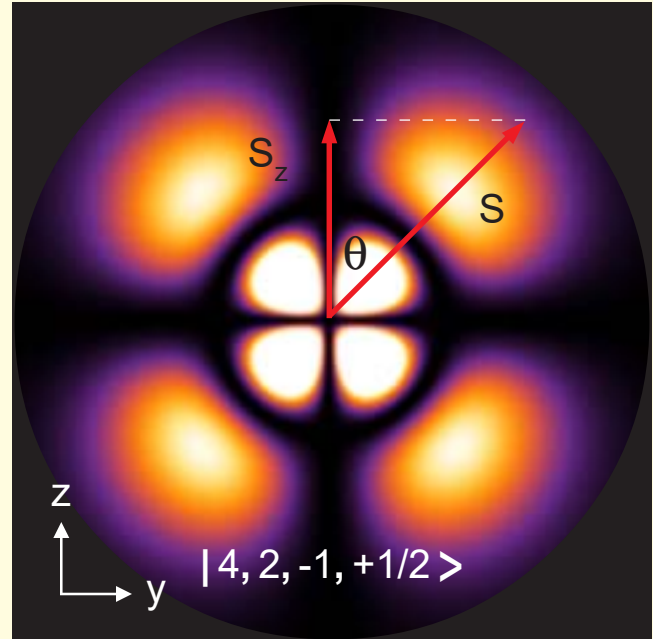
The **orbital magnetic quantum number**  $m_\ell$  ( $m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell$ ) is understood as the projection of the orbital angular momentum of the electron in a direction of spatial anisotropy (called the “z-direction”) in terms of  $\hbar$ . The z-component of the orbital angular momentum  $L_z$  of a hydrogen atom in the quantum state  $|n, \ell, m_\ell, m_s\rangle$  is  $L_z = m_\ell \hbar$  (J·s).

**example:** For the quantum state shown in the figure to the right,  $L_z = -1.000 \hbar$ . Note: since  $L = 2.449 \hbar$  and  $L_z = -1.000 \hbar$ , angle  $\theta$  would be  $65.9^\circ$ .



## SPIN QUANTUM NUMBER

The magnitude of the spin angular momentum of an electron in a hydrogen atom in any quantum state is  $S = [.5(.5 + 1)] \hbar = .866 \hbar$  (J·s). The **spin quantum number  $m_s$**  ( $m_s = \pm 1/2$ ) is understood as the projection of the spin angular momentum of the electron in a direction of spatial anisotropy (called the “z-direction”) in terms of  $\hbar$ . The z-component of the spin angular momentum  $S_z$  of a hydrogen atom in the quantum state  $|n, \ell, m_\ell, m_s\rangle$  is  $S_z = m_s \hbar$  (J·s).



**example:** For the quantum state shown in the figure above,  $S_z = +.500 \hbar$ . Note: since  $S = .866 \hbar$  and  $L_z = +.500 \hbar$ , angle  $\theta$  would be  $54.7^\circ$ .

# HYDROGEN QUANTUM STATES AND ENERGIES

	$l=0$ (s)	$l=1$ (p)	$l=2$ (d)	$l=3$ (f)	energy
n=5 (O)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2	— — — — — — — -3 -2 -1 0 +1 +2 +3	← -0.54 eV
n=4 (N)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2	— — — — — — — -3 -2 -1 0 +1 +2 +3	← -0.85 eV
n=3 (M)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2		← -1.51 eV
n=2 (L)	— 0	— — — -1 0 +1			← -3.40 eV
n=1 (K)	— 0				← -13.60 eV

# HYDROGEN SHELLS

A **shell** is the set of all quantum states for which the principal quantum number  $n$  is the same integer. For example, the set of 18 quantum states  $\{|n=3, \ell, m_\ell, m_s\rangle\}$  are said to comprise the atom's M-shell (or  $n=3$  shell).

	$\ell=0$ (s)	$\ell=1$ (p)	$\ell=2$ (d)	$\ell=3$ (f)	energy
n=4 (N)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2	— — — — — — — -3 -2 -1 0 +1 +2 +3	← -0.85 eV
n=3 (M)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2		← -1.51 eV
n=2 (L)	— 0	— — — -1 0 +1			← -3.40 eV
n=1 (K)	— 0				← -13.60 eV

## HYDROGEN SUBSHELLS

A **subshell** is the set of all quantum states for which  $n$  and  $\ell$  are the same pair of integers. For example, the set of 10 quantum states  $\{|n=4, \ell=2, m_\ell, m_s\rangle\}$  are said to comprise the atom's 4d subshell.

	$\ell=0$ (s)	$\ell=1$ (p)	$\ell=2$ (d)	$\ell=3$ (f)	energy
n=4 (N)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2	— — — — — — — -3 -2 -1 0 +1 +2 +3	← -0.85 eV
n=3 (M)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2		← -1.51 eV
n=2 (L)	— 0	— — — -1 0 +1			← -3.40 eV
n=1 (K)	— 0				← -13.60 eV

# HYDROGEN ORBITALS

An **orbital** is the set of the two quantum states ( $m_s = \pm .5$ ) for which  $n$ ,  $\ell$ , and  $m_\ell$  are the same triple of integers. For example, the set of 2 quantum states  $\{|n=3, \ell=1, m_\ell=+1, m_s = \pm .5\rangle\}$  are said to be one of the atom's 3p orbitals.

	$\ell=0$ (s)	$\ell=1$ (p)	$\ell=2$ (d)	$\ell=3$ (f)	energy
n=4 (N)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2	— — — — — — — -3 -2 -1 0 +1 +2 +3	← -0.85 eV
n=3 (M)	— 0	— — — -1 0 +1	— — — — — -2 -1 0 +1 +2		← -1.51 eV
n=2 (L)	— 0	— — — -1 0 +1			← -3.40 eV
n=1 (K)	— 0				← -13.60 eV

# DOWNWARD TRANSITION SELECTION RULES

Electrons in excited states can spontaneously make downward transitions, emitting a photon in the process. But this is only “possible” if the following selection rules are met: (1)  $\Delta l = \pm 1$  and (2)  $\Delta m_l = 0, \pm 1$ .

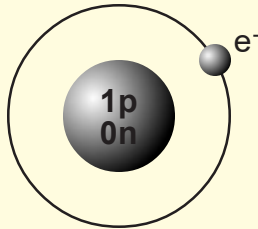
	$l=0$ (s)	$l=1$ (p)	$l=2$ (d)	$l=3$ (f)	energy
n=4 (N)	$\frac{\text{---}}{0}$	$\frac{\text{---}}{-1} \frac{\text{---}}{0} \frac{\text{---}}{+1}$	$\frac{\text{---}}{-2} \frac{\text{---}}{-1} \frac{\text{---}}{0} \frac{\text{---}}{+1} \frac{\text{---}}{+2}$	$\frac{\text{---}}{-3} \frac{\text{---}}{-2} \frac{\text{---}}{-1} \frac{\text{---}}{0} \frac{\text{---}}{+1} \frac{\text{---}}{+2} \frac{\text{---}}{+3}$	← -0.85 eV
n=3 (M)	$\frac{\text{---}}{0}$	$\frac{\text{---}}{-1} \frac{\text{---}}{0} \frac{\text{---}}{+1}$	$\frac{\text{---}}{-2} \frac{\text{---}}{-1} \frac{\text{---}}{0} \frac{\text{---}}{+1} \frac{\text{---}}{+2}$		← -1.51 eV
n=2 (L)	$\frac{\text{---}}{0}$	$\frac{\text{---}}{-1} \frac{\text{---}}{0} \frac{\text{---}}{+1}$			← -3.40 eV
n=1 (K)	$\frac{\text{---}}{0}$				← -13.60 eV



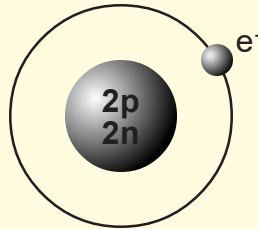
# HYDROGEN-LIKE ATOMS

A hydrogen-like atom is any atom which has a single electron (regardless of the number of protons or neutrons in the nucleus). Examples are shown:

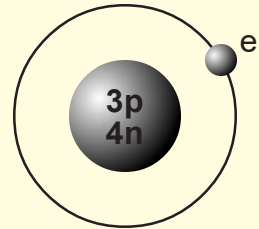
neutral protium ( ${}^1\text{H}$ )



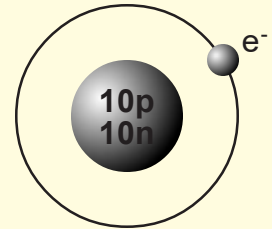
singly-ionized helium ( ${}^4\text{He}^+$ )



doubly-ionized lithium ( ${}^7\text{Li}^{+2}$ )



9/fold-ionized neon ( ${}^{20}\text{Ne}^{+9}$ )



The allowed energies for a quantum mechanical hydrogen-like atom are:

$$E_n = (-13.6 \text{ eV})Z^2/n^2$$

where  $Z$  is the atomic number and  $n$  is the principal quantum no. (1, 2, ...)

atom $\rightarrow$	${}^1\text{H}$	${}^4\text{He}^+$	${}^7\text{Li}^{+2}$
$E_4 =$	-0.9	-3.4	-7.7
$E_3 =$	-1.5	-6.0	-13.6
$E_2 =$	-3.4	-13.6	-30.6
$E_1 =$	-13.6	-54.4	-122.4

# SKEWING OF SUBSHELL ENERGIES IN MULTI-ELECTRON ATOMS

n=5

(O)

—  
0

— — —  
-1 0 +1

— — —  
-1 0 +1

— — — — —  
-2 -1 0 +1 +2

— — — — —  
-2 -1 0 +1 +2

n=4

(N)

—  
0

— — —  
-1 0 +1

— — — — —  
-2 -1 0 +1 +2

n=3

(M)

—  
0

— — —  
-1 0 +1

n=2

(L)

—  
0

n=1

(K)

—  
0

— — — — —  
-3 -2 -1 0 +1 +2 +3

— — — — —  
-3 -2 -1 0 +1 +2 +3

# THE PAULI EXCLUSION PRINCIPLE

The **Pauli Exclusion Principle** states that two or more fermions (particles, like electrons, with half-integer spins) in a quantum system cannot occupy the same quantum state (have the same set of quantum numbers) simultaneously. This principle was formulated by Austrian physicist Wolfgang Pauli in 1925 and was originally applied to electrons in poly-electronic atoms. Later Pauli extended this principle to apply to all fermions in any quantum system with his **spin-statistics theorem** in 1940.

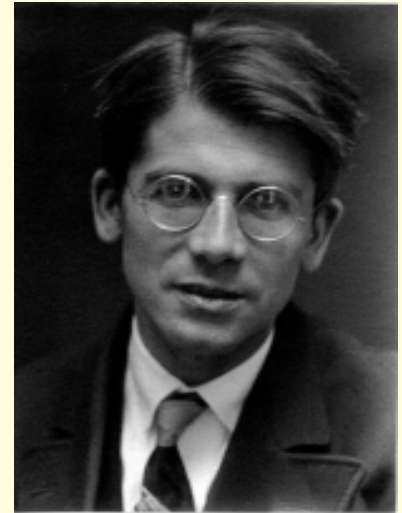


Wolfgang Pauli  
(1900-1958)

# HUND'S RULE

The filling order of equal energy orbitals is such that the number of electrons with unpaired spins is maximized. Due to German physicist Friedrich Hund (1927). Ground state configuration examples:

	1s	2s	2p			
<b>B</b>	↑↓	↑↓	↑			$1s^2 2s^2 2p^1$
<b>C</b>	↑↓	↑↓	↑	↑		$1s^2 2s^2 2p^2$
<b>N</b>	↑↓	↑↓	↑	↑	↑	$1s^2 2s^2 2p^3$
<b>O</b>	↑↓	↑↓	↑↓	↑	↑	$1s^2 2s^2 2p^4$
<b>F</b>	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^5$
<b>Ne</b>	↑↓	↑↓	↑↓	↑↓	↑↓	$1s^2 2s^2 2p^6$



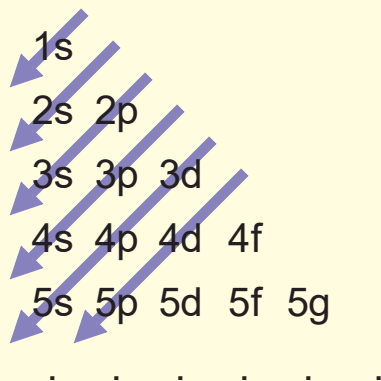
Friedrich Hund  
(1896-1997)

# ELECTRON CONFIGURATION

**Electron configuration** is a notation used to represent the subshell populations of electrons in an atom in its ground state. In this notation an integer (indicating the shell) is followed by a lower case letter (indicating the subshell) with a following superscript (indicating the number of electrons populating that subshell). For example,  $3p^5$  indicates 5 electrons populating the 3p-subshell. Subshell designations should be listed in order of increasing energy. The filling order of electrons (increasing energy) is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < \dots$$

order of filling  
mnemonic →



# GROUND STATE ELECTRON CONFIGURATIONS

atomic number	chemical symbol	ground state configuration	ionization energy (eV)
1	H	$1s^1$	13.60
2	He	$1s^2$	24.58
3	Li	$1s^2 2s^1$	5.39
4	Be	$1s^2 2s^2$	9.32
5	B	$1s^2 2s^2 2p^1$	8.30
6	C	$1s^2 2s^2 2p^2$	11.26
7	N	$1s^2 2s^2 2p^3$	14.55
8	O	$1s^2 2s^2 2p^4$	13.61
9	F	$1s^2 2s^2 2p^5$	17.42
10	Ne	$1s^2 2s^2 2p^6$	21.56
11	Na	$1s^2 2s^2 2p^6 3s^1$ or [Ne]3s <sup>1</sup>	5.14
12	Mg	$1s^2 2s^2 2p^6 3s^2$ or [Ne]3s <sup>2</sup>	7.64
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$ or [Ne]3s <sup>2</sup> 3p <sup>1</sup>	5.98
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$ or [Ne]3s <sup>2</sup> 3p <sup>2</sup>	8.15
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$ or [Ne]3s <sup>2</sup> 3p <sup>3</sup>	10.48