Quantum Numbers

The energy eigenstates of the hydrogen atom are states of definite energy, magnitude of angular momentum, and z component of angular momentum. The values of those quantities are labeled by the quantum numbers n, l, and m_l , respectively. These three quantum numbers must be integers, and the spin quantum number m_s must be -1/2 (spin-up) or -1/2 (spin-down). Other restrictions are given below.

Letter	Name	Range	Physical interpreta-
			tion
n	Principal quan-	$1 \le n < \infty$	$E_n = -(1/n^2)Ry,$
	tum number		with $(1 Ry \approx 13.6)$
			eV)
l	Angular momen-	$0 \le l \le n-1$	$ \overrightarrow{L} = \sqrt{l(l+1)}\hbar$
	tum quantum		
	number		
m_l	Magnetic quan-	$-l \le m_l \le l$	$L_z = m_l \hbar$
	tum number		
m_s	Spin quantum	$m_s = \pm 1/2$	$S_z = m_s \hbar$
	number		

Principal Quantum Number n. The term "principal quantum number" refers to the fact that n determines energy: each eigenstate ψ_{nlm_l} has energy $E_n = -(1/n2)$ Ry, where 1 Ry ≈ 13.6 eV is a unit of energy called a "rydberg." So the ground state of hydrogen has energy -1 Ry \approx -13.6 eV, the first excited state has energy -(1/4) Ry \approx -3.4 eV, and so on.

Angular Momentum Quantum Number l. l controls the magnitude of the total angular momentum of the electron about the nucleus is $L = \sqrt{l(l+1)}\hbar$.

Magnetic Quantum Number m_l . While l determines the magnitude of the angular momentum vector, m_l determine the z component of the angular momentum $L_z = m_l \hbar$. The name comes from the fact that the simplest way to measure a particular component of the angular momentum of a charged particle is to measure the magnetic field it creates.

Spin m_s . In 1924 Pauli suggested that each electron in an atom has a fourth quantum number that can only take on two possible values. He gave no physical explanation for this new electron property, which he called a "two-valuedness not describable classically." Consider a ball spinning about its own axis, except it is not a ball and it is not spinning.

For every electron, the magnitude of spin is $\sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$, with values of -1/2 or +1/2. The z component of the spin is therefore $L_z = m_s \hbar = \pm (1/2)\hbar$.

Any particle with half-integer spin is a fermion, for example electrons, protons, and neutrons. Any particle with integer spin is a boson, for example photons. Every particle can be classified as either a "fermion," meaning it obeys the Pauli exclusion principle, or a "boson," meaning it does not.

The energy eigenvalues of a hydrogen atom depend only on n (to a very good approximation). The following formulas use m_e and e for the electron mass and charge, respectively

$$\begin{split} E_n &= -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{1}{2n^2} m_e c^2 \alpha^2 = -\frac{1}{n^2} \mathrm{Ry} \\ &= -\frac{1}{n^2} 13.6 \mathrm{eV} = \frac{1}{n^2} 2.18 \times 10^{-18} \mathrm{J} \end{split}$$

where α is fine structure constant

$$\alpha \equiv \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

For a hydrogen-like atom with Z protons and one electron, the energies are

$$E_n - \frac{Z^2}{n^2} \mathrm{Ry}$$

Spectroscopic Notation

For many purposes the energy and total angular momentum of a state are more important than its orientation, so an atomic state is often designated by its values of n and l. Each value of n is called a "shell," while each combination of n and l is called a "subshell." For example, the n=2 shell consists of the subshells 2s and 2p. For example, the ground state of nitrogen Z=7 is written $1s^22s^22p^3$ to indicate that it has two electrons in the state n=1, l=0, two electrons in the state n=2, l=0, and three electrons in the state n=2, l=1.

Energies of Different Quantum State

Pauli exclusion principle. Pauli exclusion principle forbid two or more of the same type of fermion in the same quantum state as each other. That means that, in the ground state of a multielectron atom, the Z electrons (fermion) fill up the Z lowest-energy states.

n + l rule. Given two states ψ_{nl} , the subshell with the lower sum n + l will fill up first. In the case of a tie, the lower-n state fills first.

Hund's Rule. Because each electron can have spin up or spin down, two electrons can be in each combination of n, l, and m_l . That in turn means each subshell consists of 2(2l+1) degenerate states, with

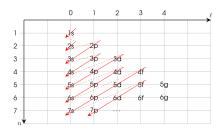


Figure: Perhabs the more familiar name for n + l rule is Aufbau rule

 $2n^2$ degenerate state for each shell. Within a particular subshell, the electrons tend to end up in the states that minimize the energy level. Two nearby electrons whose spins are identical will be, on average, farther apart from each other than if they have opposite spins. The result is that electrons with identical spins shield each other from the nucleus less than electrons with different spins, so same-spin is a lower energy state than opposite-spin.

Electron Screening Model

Consider lithium (Z=3), which in its ground state has two electrons in the 1s subshell and one in the 2s subshell. We the approximate two inner electrons as uniform spherical shells of negative charge at the Bohr radius a_0 . Approximation it feels a net charge of +e coming from the nucleus. We say that the inner electrons "screen" the nuclear charge.

According to this model, the outer electron in lithium should be just like a 2s electron in hydrogen. So the model predicts that the "ionization energy" of lithium should be

$$E = \frac{Z_{\text{eff}}^2}{n^2} 13.6 \text{ eV} = 3.4 \text{ eV}$$

Periodic Table

Noble gases 18	2 Helium	10	Ne	18	Argon	36	Kr	Crypton	54	Xe	Xenon	98	Rn	Radon	118	og O	oganesson
	Halogens 17	6	F	17	Chlorine	35	Br	Bromine	53	ı	Iodine	85	At	Astatine	117	Ts	Tennessine o
	H 91	8	0	16	Sulfur	34	Se	Selenium	52	Te	Tellurium	84	Po	Polonium	116	Lv	ivermorium
	15	7	Z	115	Phosphorus	33	As	Arsenic	51	Sb	Antimony	83	Bi	Bismuth	115	Mc	Flerovium Moscovium Livermorium
	14	9	ပ	14	Silicon	32	Ge	Germanium	95	Sn	Tin	82	Pb	Lead	114	H	
	13	2 2	0	3p 13	Aluminum	31	4p Ga	Gallium		uI de	Indium	81	LL do	Thallium		Nh Nh	Nihonium
		C	4,	60		_	4,		_ '	o		_ `	<u>ه</u>			<u>``</u>	
					12	30	Zu	Zinc	48	S	Cadmium	80	Hg	Mercury	112	C	Copernicium
					11	29	 C	Copper $[Ar]4s3d^{10}$	47	Ag	Silver [Kr]5s4d ¹⁰	79	γn	Gold [Xe]6s4f ¹⁴ 5d ¹⁰	111	Rg	Roentgenium
	ions are eyond it.				10	28	ï	Nickel	46	Pd	Palladium $[Kr]4d^{10}$	78	Pt	Platinum [Xe]6s4f ⁴⁴ 5d ⁹	110	Ds	Meitnerium Darmstadtium
	The excepti ns added bo				6	27	ి	Cobalt	45	Rh	Rhodium [Kr]5s4d ⁸	77	ı,	Iridium	109	Mt	Meitnerium
tter for l.	n + l rule. ' he electroi n.)	` -	al	Transition metals	8	76	Fe	Iron	44	Ru	Ruthenium [Kr]5s4d ⁷	9/	ő	Osmium	108	Hs	Hassium
n and a le	ng to the gas plus t	,	: Non-Metal	Transitio	^	25	Mn	Manganese	43	Ľ	Technetium	75	Re	Rhenium	107	Bh	Bohrium
umber for 3)	in accordi ious noble have a sing				9	24	Ċ	Chromium $[Ar]4s3d^5$	42	Mo	Molybdenum $[Kr]5s4d^5$	74	×	Tungsten	106	Sg	Seaborgium
d with a nu = 2), $f(l = 1)$	g the previperscript	- I	: Metalloid		5	23	>	Vanadium	41	S	Niobium [Kr]5s4d ⁴	73	Та	Tantalum	105	Dp	Dubnium
ell is labele l $l = 1$, $d(l = 1)$	on configur ow, showin without a su				4	22	Ξ	Titanium	40	Zr	Zirconium	72	Hf	Hafnium	104	Rf	Rutherfordium
Each subshell is labeled with a number for n and a letter for l s $(l=0), p$ $(l=1), d$ $(l=2), f$ $(l=3)$	Most electron configurations fill in according to the $n+l$ rule. The exceptions are marked below, showing the previous noble gas plus the electrons added beyond it. (Subshells without a superscript have a single electron.)	; ;	: Metal		3	21	Sc	Scandium	39	Y	Yttrium	71	Γn	Lutetium	103	Lr	Lawrencium F [Rn]7.8 ² 5/4 ⁷ 7p
			_			34			44			54			<i>p</i> 9		
													Lan	thanides	T	Act	tinides
	Alkaline earths 2	4	Beryllinm	12	Magnesium	20	Ca	Calcium	38	Sr	Strontium	99		Barium	88	Ra	Radium
Alkali 1	1 H Hydrogen		: E		Sodium	19		Potassium	37		Rubidium	55	ర	Cesium	87	Ŧ	7s Francium
	18		2s	ć	ŝ		45			55				9			7.8

Lanthanides	22	28	59	09	19	62	63	49	65	99	29	89	69	_
(rare earths)	La	ಶ	. A	PN	Pm	Sm	En	PS	TP	Dy	Ho	Er	Tm	
44	4f Lanthanum	-	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	
,	$[Xe]6s^25d$	$[Xe]6s^24f5d$						[Xe]6s ² 4f ⁷ 5d						
Actinides	l	06	91	92	93	94	95	96	26	86	66	100	101	
<i>f</i> 2	Ac	Th	Pa	n	ď	Pu	Am	Cm	Bk	Ç	Es	Fm	Md	
ę.		Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendeleviur	
	$[Rn]7s^26d$	$[Rn]7s^{2}6d^{2}$	$[Rn]7s^25f^26d$	$[Rn]7s^{2}5f^{3}6d$	[Rn]7s ² 5f ⁴ 6d			$[Rn]7s^25f^76d$						_

Figure: Periodic table

Energy Eigenstates

The energy eigenstates of the hydrogen atom are of the form

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_l^{m_l}(\theta,\phi).$$

A full specification of the quantum state of a hydrogen atom also includes the spin state (up or down) of the electron.

Radial Wavefunction

The radial wavefunction is given by the following:

$$R_{nl}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \left(\frac{2r}{na_0}\right)^l \exp\left(-\frac{r}{na_0}\right) L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right)}$$

where L is called an associated Laguerre polynomial and is defined as

$$L_n^k(x) = (-1)^k \left(\frac{d}{dx}\right)^k \left[e^x \frac{d^{p+k}}{dx^{p+k}} \left(e^{-x} x^{p+k} \right) \right]$$

As you know, k=0 then the above formula calls for the "zeroth derivative," or the function itself. $R_{nl}(r)$ is a polynomial in r times a decaying exponential $e^{-r/(a_0n)}$, where a_0 is a constant called the "Bohr radius"

$$a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 5 \times 10^{-11} \text{ m}$$

Here's first few Radial Wavefunctions: for n = 1

$$R_{1,0} = 2a_0^{-3/2} \exp\left(-\frac{r}{a_0}\right)$$

for n=2

$$\begin{split} R_{2,0} &= \frac{1}{\sqrt{2}} a_0^{-3/2} \left(1 - \frac{r}{2a_0} \right) \exp \left(-\frac{r}{2a_0} \right) \\ R_{2,1} &= \frac{1}{\sqrt{24}} a_0^{-3/2} \frac{r}{a_0} \exp \left(-\frac{r}{2a_0} \right) \end{split}$$

for n=3

$$R_{3,0} = \frac{2}{\sqrt{27}} a_0^{-3/2} \left[1 - \frac{2r}{3a_0} + \frac{2}{27} \left(\frac{r}{a_0} \right)^2 \right] \exp\left(-\frac{r}{3a_0} \right)$$

$$R_{3,1} = \frac{8}{27\sqrt{6}} a_0^{-3/2} \left(1 - \frac{r}{6a_0} \right) \frac{r}{a_0} \exp\left(-\frac{r}{3a_0} \right)$$

$$R_{3,2} = \frac{4}{81\sqrt{30}} a_0^{-3/2} \left(\frac{r}{a_0} \right)^2 \exp\left(-\frac{r}{3a_0} \right)$$

Spherical Harmonics

Spherical harmonics are products of complex exponentials in ϕ and polynomials in $\cos \theta$:

$$Y_l^{m_l}(\theta, \psi) = \pm \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m_l|)!}{(l+|m_l|)!}} P_l^{m_l}(\cos \theta) \exp(im_l \phi)$$

where l and m_l are integers and $-l \leq m_l \leq l$. The plus minus comes from +1 for all negative m_l and all even values of m_l , and -1 for odd positive values. So the only differences between $Y_l^{m_l}$ and and Y_l^{-ml} are that they have different signs if m_l is odd, and the exponent in $e^{im_l\phi}$ changes sign between them. Also, P is an "associated Legendre polynomial"

$$P_{l}^{m_{l}}(x) \equiv (1 - x^{2})^{|m_{l}|/2} \left(\frac{d}{dx}\right)^{|m_{l}|} \left[\frac{1}{2^{l} l!} \left(\frac{d}{dx}\right)^{l} (x^{2} - 1)^{l}\right]$$

Not to be confused by Legendre polynomials (defined by Rodrigues formula)

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l (x^2 - 1)^l$$

 $Y_l^{m_l}$ is a polynomial in $\sin \theta$ and $\cos \theta$ multiplied by $e^{im_l\phi}$. Here's first few Spherical Harmonics: for l=0

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

for l=1

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$$
$$Y_0^{\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

for l=2

$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$$

$$Y_2^0 = \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm 2i\phi}$$

$$Y_2^0 = \sqrt{\frac{15}{31\pi}} \sin^2\theta e^{\pm 2i\phi}$$

Probability Distributions

For any particle with wavefunction Ψ in 3D, the probability per unit volume of finding the particle in a given region is $|\Psi|2$. For an electron in a hydrogen atom energy eigenstate ψ_{nlm_l} , probability of finding the electron between radii r_1 and r_2

$$P(r_1 \le r \le r_2) = \int_{r_1}^{r_2} r^2 R^2 dr$$

while the probability of finding the electron in a specified range of angles is

$$\int_{\theta_1}^{\theta_2} \int_{\phi_1}^{\phi_2} \sin\theta |Y_l^{m_l}|^2 d\psi d\theta$$

These integrals are normalized so that

$$\int_{0}^{\infty} r^{2} R^{2} dr = \int_{0}^{\pi} \int_{0}^{2\pi} \sin \theta |Y_{l}^{m_{l}}|^{2} d\psi d\theta = 1$$

Zeeman Effect

The Zeeman effect refers to the changes in atomic spectra caused by an external magnetic field. In classical electrodynamics, magnets tend to align with magnetic fields, or magnet pointing along an external magnetic field has less energy than one pointing opposite to the external field. Because an electron is negatively charged, its magnetic moment points opposite to its angular momentum. So a positive m_l means its magnetic moment is pointing opposite external field, if we define positive z axis as the direction of external field. A negative m_l means the electron's magnetic field is pointing with the external field, which is the preferred (low-energy) orientation.

Therefore, in an external magnetic field pointing in the positive z direction, higher m_l leads to higher energy. For weak magnetic fields (neglecting spin), the Zeeman contribution to the energy of a state is

$$\Delta E = m_l \mu_B B$$

where μ_B is Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e}$$

If an atom transitions between states in which all its electron spins cancel, then you can ignore spin. In that case the splitting caused by a magnetic field is called the "normal Zeeman effect." in the presence of an external magnetic field, the normal Zeeman effect splits the n=2 to n=1 transition into three separate transitions based on Δm_l . The selection rule limits which electron transitions generally occur

$$\Delta l = \pm 1$$

$$\Delta m_l = -1, 0, 1$$