Chapter L

Atomic Physics

Blinn College - Physics 1402 - Terry Honan

L.1 - Early Models of the Atom

Dalton, Thomson and Rutherford

Although speculation about atoms goes back to the Greek philosophers, the notion of atoms was not a scientifically significant notion until the nineteenth century. Dalton was a chemist who early in the century introduced the idea of the atom to explain the recombination behavior of compounds in chemistry. Atoms are basic building blocks of matter that have different masses and sizes and can recombine to form different compounds. Mass is conserved and the masses of compounds correspond to summing all the masses in the constituent atoms. This was very much on the mark for the purposes of chemistry.

Early in the nineteenth centuries physicists were thinking more of continuous ideas of matter and not in terms of discrete fundamental units. Progress in thermodynamics and in relating macroscopic thermodynamic quantities to microscopic laws led physicist to start thinking seriously about atoms. J.J. Thomson discovered the electron in 1897 when studying cathode rays, beams emanating from cathodes, or negative terminals. He found the charge to mass ratio of the particles in the cathode rays and saw that different materials produced identical particles in cathode rays.

Thomson tried to model how different atoms could possess the same electrons. He modeled atoms as continuous blobs of positive charge with negatively charged electrons distributed throughout the positively charged background. This was given the ludicrous nickname of the "plum pudding model."

Rutherford performed an experiment to probe Thomson's atoms by shooting alpha particles at thin gold foil. Alpha particles are particles emitted from some radioactive materials. We now know they are the nucleus of helium atoms. When these heavy particles were shot through gold foil, Rutherford expected them to pass through only slightly deflected or slowed. What he observed was that most were undeflected but a few were scattered at large angles and some were scattered backward. Rutherford was shocked at his result; he likened it to tissue paper reflecting a shell. He correctly interpreted his results as atoms having a very dense core, a nucleus, instead of being uniformly dense. With this he discovered the atomic nucleus. It is ironic that he discovered the nucleus using nuclei, alpha particles, but alpha particles had not been identified as nuclei at the time.

Rutherford then modeled the atom as very dense cores, nuclei, surrounded by a very diffuse density of electrons orbiting, somehow. This had an obvious theoretical problem. The electrons would have to be moving to prevent being pulled into the positively charged nuclei, so if they orbited, then the accelerating charges wold radiate energy and collapse into the nucleus. Rutherford's atoms were unstable.

Atomic Spectra and the Hydrogen Spectrum

Hot materials produce a continuous spectrum that approximates the idealized black body spectrum. Individual atoms produce a very different pattern. When the spectrum of a hot cloud of diffuse atoms is viewed there is a discrete pattern of lines, the atomic spectra. The characteristic pattern of lines identifies the atoms.

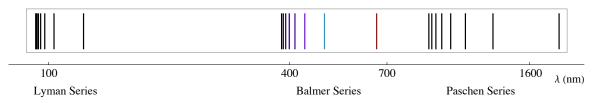
The atomic spectrum of hydrogen were observed to have a characteristic pattern; the inverse wavelength $1/\lambda$ satisfies

$$\frac{1}{\lambda} = R\left(\frac{1}{n'^2} - \frac{1}{n^2}\right) \text{ where } n' = 1, 2, 3, \dots \text{ and } n = n' + 1, n' + 2, \dots$$

where R is the Rydberg constant.

$R = 1.097 \times 10^7 \text{ m}^{-1}$

The different values for n' = 2 are in the visible spectrum and are called the Balmer series. The part of the spectrum corresponding to n' = 3 are in the infrared part of the spectrum and is known as the Paschen series and the n' = 1 lines are the Lyman series in ultraviolet.



Example L.1 - Minimum and Maximum Wavelengths in a Series

What are the minimum and maximum wavelengths in the Lyman, Balmer and Paschen Series

Solution

We need the value of the Rydberg constant.

$$R = 1.097 \times 10^7 \text{ m}^{-1}$$

Because of the left-hand side of the Rydberg formula is $1/\lambda$, the larger the difference in the *n* values, the smaller the wavelength.

For the Lyman series n' = 1 so the largest wavelength is n = 2

$$\frac{1}{\lambda_{\max}} = R \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \implies \lambda_{\max} = 1.21 \times 10^{-7} \,\mathrm{m} = 121 \,\mathrm{nm}$$

As *n* gets larger, λ gets smaller. There is not precisely a smallest wavelength in the series but there is a lower limit on the values. As $n \to \infty$ then $1/n \to 0$ and we refer to this lower limit as the smallest.

$$\frac{1}{\lambda_{\min}} = R\left(\frac{1}{1^2} - 0\right) \implies \lambda_{\min} = 9.12 \times 10^{-8} \text{ m} = 91.2 \text{ nm}$$

For the Balmer series with n' = 2 so the largest wavelength is n = 3

$$\frac{1}{\lambda_{\text{max}}} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \implies \lambda_{\text{max}} = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}$$

and the smallest is the limit as $n \rightarrow \infty$ as with the Lyman series

$$\frac{1}{\lambda_{\min}} = R\left(\frac{1}{2^2} - 0\right) \implies \lambda_{\min} = 3.64 \times 10^{-7} \text{ m} = 364 \text{ nm}$$

For the Pashen series with n' = 3 so the largest wavelength is n = 4

$$\frac{1}{\lambda_{\max}} = R \left(\frac{1}{3^2} - \frac{1}{4^2} \right) \implies \lambda_{\max} = 1.87 \times 10^{-6} \text{ m} = 1880 \text{ nm}$$

and the smallest is the limit as $n \to \infty$ as with the Lyman series

$$\frac{1}{\lambda_{\min}} = R\left(\frac{1}{3^2} - 0\right) \implies \lambda_{\min} = 8.20 \times 10^{-7} \text{ m} = 820 \text{ nm}$$

The Bohr Atom

The frequencies of sound that come from a musical instrument correspond to internal frequencies of vibration in the instrument; a note produced by a guitar or piano corresponds to a frequency of vibration of a string. It was not possible to understand the spectrum of light from an atom in a similar way. Bohr considered how to apply some notion of quantization to an atom in a way that was consistent with Einstein's photon hypothesis, that could explain the atomic spectra and remove the instability of the Rutherford atom.

What Bohr got correct was: Atoms have certain discrete energy levels or states that are, for some yet unknown reason, stable. The spectrum of radiation produced by atoms corresponds to photons whose energy is equal to the energy difference between the energy levels. Suppose an atom in a state with energy E_i transitions to a lower energy level E_f then a photon is emitted with the energy

$$E_{\text{photon}} = h f = E_i - E_f.$$

Quantization of Angular Momentum

Bohr tried to find some rule to describe the energy levels. Planck's constant has units of angular momentum. This likely motivated Bohr to try a rule that involved the quantization of angular momentum. Bohr focused on a model, analogous to the solar system, where electrons move in circular orbits. He applied this idea to the hydrogen atom and other one-electron atoms, like ionized helium He⁺ with atomic number Z = 2, twice ionized lithium Li⁺⁺ with atomic number Z = 3, etc. The angular momentum of an electron in a circular orbit of radius *r* with speed *v* is $L = r m_e v$. He then assert his quantization rule that this angular momentum was quantized in integer multiples of Planck's constant divided by 2π . The *n*th state satisfies

$$L_n = r_n m_e v_n = n \frac{h}{2\pi}$$
 where $n = 1, 2, 3, ...$

Newton's Second Law

For a circular orbit we can apply Newton's second law to relate the radius and speed. The acceleration is centripetal (or radial) and has the value, as you saw in Physics I, of $a_c = v^2/r$. The force of a nucleus with positive charge Ze on the electron with charge -e is toward the center with magnitude $F = k Ze^2/r^2$, where r is the distance between the two, the radius of the orbit. Now apply the second law

$$F = m_e a_c \implies k \frac{Ze^2}{r^2} = m_e \frac{v^2}{r} \implies k \frac{Ze^2}{r} = m_e v^2$$

Radius of the *n*th Level Orbit

The angular momentum quantization condition allows us to write the speed in terms of the radius and n.

$$L_n = r_n m_e v_n = n \frac{h}{2\pi} \implies v_n = n \frac{h}{2\pi m_e r_n}$$

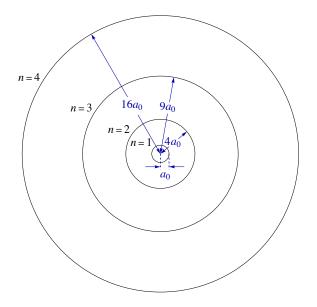
Insert this into our expression from the second law for the n^{th} level gives

$$k \frac{Ze^2}{r_n} = m_e v_n^2 \implies k \frac{Ze^2}{r_n} = m_e \left(\frac{n h}{2\pi m_e r_n}\right)^2 \implies r_n = \frac{h^2}{4\pi^2 m_e k Ze^2} n^2$$

Define the Bohr radius a_0 as the radius of the ground state with n = 1, for hydrogen with Z = 1.

$$r_n = a_0 \frac{n^2}{Z}$$
 where $a_0 = \frac{h^2}{4\pi^2 m_e k e^2} = 5.29 \times 10^{-11} \text{ m}$

This sets the scale for the size of atoms.



Energy of the *n*th Level

We now need a formula for the energy of a circular orbit in terms of the radius. The kinetic energy is $K = \frac{1}{2} m_e v^2$ and the potential energy is $U = kq_1 q_2/r = -kZe^2/r$.

$$E = K + U = \frac{1}{2}m_e v^2 - k\frac{Ze^2}{r}$$

Now use the formula from the second law that relates speed to radius.

$$k \frac{Ze^2}{r} = m_e v^2 \implies E = \frac{1}{2} m_e v^2 - k \frac{Ze^2}{r} = \frac{1}{2} k \frac{Ze^2}{r} - k \frac{Ze^2}{r} = -\frac{1}{2} k \frac{Ze^2}{r}$$

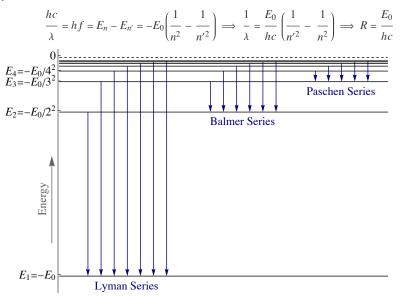
Using the radius of the n^{th} level we get its energy.

$$E_n = -\frac{2\pi^2 m_e k^2 Z^2 e^4}{h^2 n^2} = -E_0 \frac{Z^2}{n^2} \text{ where } E_0 = \frac{2\pi^2 m_e k^2 e^4}{h^2} = 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$$

 E_0 is the ionization energy for hydrogen, the energy needed to remove the electron from the ground state, the n = 1 state.

The Spectrum of Hydrogen

Recall Bohr's assumption that when an electron transitions between two energy levels, the photon acquires the energy difference between the levels, $E_{photon} = h f = E_i - E_f$. This gives the Rydberg spectrum. In a transition between E_n and $E_{n'}$ we have



Summary of the Bohr Atom

The Right Part

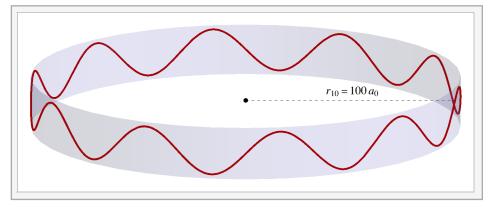
- Atoms have discrete energy levels.
- When an electron undergoes a transition from a higher energy level to a lower one, it emits a photon which has the energy difference between the levels.
- The Wrong Part
 - Electrons do not move in a circular orbit or in any precisely defined path. That violates the uncertainty principle.
 - Although angular momentum is quantized, it is quantized in a quite different way. Bohr atoms would have huge angular momenta and would then also have huge magnetic moments.
 - Bohr had only one quantum number *n*. It turns out there are four.
 - The Bohr model could not describe multi-electron atoms
- The Lucky Part
 - Although, in retrospect, his reasoning was not correct, he happened to get the correct energy levels for hydrogen and other singleelectron atoms.
 - Because he had the correct energy levels, he was able to correctly describe the spectrum of hydrogen and other single electron atoms.

de Broglie Standing Waves

When de Broglie introduced his matter wave hypothesis, he referred to the Bohr atom. Bohr's quantization condition could be interpreted as a standing wave of an electron with wavelength $\lambda = h/p$. There is constructive interference of *n* full wavelengths around one circumference, $2\pi r$

$$2\pi r = n\lambda = n \frac{h}{p} = n \frac{h}{m_e v} \implies rm_e v = n \frac{h}{2\pi}$$

Using $\lambda = h/p$ and $p = m_e v$ we then get Bohr's quantization condition.



de Broglie's interpretation of the Bohr quantization condition as a standing wave (constructive interference) of matter waves

The Bohr atom with de Broglie's matter wave interpretation is no less wrong. However, de Broglie gave an important insight that led to the development of the proper wave equation needed for understanding atoms.

Example L.2 - Twice Ionized Lithium

Twice ionized lithium Li^{++} is a one electron atom with a charge of +3e in the nucleus.

(a) How much energy (in eV) does it take to remove the one electron left?

Solution

We just need to use Z = 3 and the formulas given.

$$E_n = -E_0 \frac{Z^2}{n^2}$$
 where $E_0 = 13.6 \text{ eV}$

The ionization energy is then $-E_1$ with Z = 3.

$$-E_1 = +E_0 \ 3^2 = 122 \ \text{eV}$$

(b) In twice ionized lithium, what is the energy (in joules) of the photon emitted when the electron undergoes a transition from the fifth to the second energy levels? Also what are the frequency and wavelength of the photon?

Solution

Here we will use the same energy formula with

$$E_n = -E_0 \frac{Z^2}{n^2}$$
 where $E_0 = 2.18 \times 10^{-18} \text{ J}$

The energy of the photon is

$$E = E_i - E_f = E_5 - E_2 = -E_0 3^2 \left(\frac{1}{5^2} - \frac{1}{2^2}\right) = 4.12 \times 10^{-18}$$

To find the frequency use E = hf

$$h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \implies f = E/h = 6.22 \times 10^{15} \text{ Hz}$$

and $f\lambda = c$ gives the wavelength.

$$c = 3.00 \times 10^8 \text{ m/s} \implies \lambda = c/f = 4.82 \times 10^{-8} \text{ m} = 48.2 \text{ nm}$$

Example L.3 - The *n* = 5 Bohr Orbit

For the n = 5 Bohr orbit for hydrogen, what is the radius, speed and de Broglie wavelength of the electron?

Solution

$$r_n = a_0 \frac{n^2}{Z}$$
 where $a_0 = \frac{h^2}{4\pi^2 m_e k e^2} = 5.29 \times 10^{-11} \text{ m}$

Here we have Z = 1 and n = 5.

$$r_n = a_0 \frac{5^2}{1} = 1.32 \times 10^{-9} \,\mathrm{m}$$

To find the speed we use Bohr's quantization condition.

$$L_n = r_n m_e v_n = n \frac{h}{2\pi} \implies v_n = n \frac{h}{2\pi r_n m_e} = 4.28 \times 10^5 \text{ m/s}$$

There are many inter-related expressions and that means there are many ways to calculate things. The de Broglie wavelength is most simply found using $2\pi r = n\lambda$.

$$2 \pi r_n = n \lambda_n \implies \lambda_n = \frac{2 \pi r_n}{n} = 1.66 \times 10^{-9} \text{ m}$$

L.2 - The Quantum Theory of the Hydrogen Atom

Quantum Mechanics and the Schrodinger Equation

If it were not for Einstein, relativity would have emerged gradually over a period of many years, with different physicists adding their own small contributions. In the end, after a long process relativity would have emerged in essentially its modern form but the process would have probably been quite laborious. Quantum mechanics followed that laborious route. Over a period of several years after de Broglie's key insight, many physicists working from several different angles put together what became our modern theory of quantum mechanics. The two most notable contributors to this were Werner Heisenberg with what was known at the time as matrix mechanics and Erwin Schrodinger with his wave mechanics but neither of them had complete theories. Schrodinger, for instance, had his wave function but really didn't understand its probability interpretation at first; that probability interpretation came for Max Born.

The Schrodinger wave function is a complex-number valued that when squared, in the appropriate complex way, gives the probability of particle being at some position. The atom is no longer viewed as electrons in orbits but instead electrons forming probability clouds.

The Quantum Numbers

Instead of the one quantum number *n* in the Bohr atom the quantum mechanical hydrogen atom has four. To label an electron state one must give four numbers: n, ℓ , m_ℓ and m_s . It turns out that the hydrogen energy only depends on the principal quantum number *n*.

The Principal Quantum Number - n

The energy only depends on the principal quantum number n which has positive integer values.

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

The energy of the n^{th} state is the came as with the Bohr atom.

$$E_n = -\frac{2\pi^2 m_e k^2 Z^2 e^4}{h^2 n^2} = -E_0 \frac{Z^2}{n^2} \text{ where } E_0 = \frac{2\pi^2 m_e k^2 e^4}{h^2} = 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$$

The Orbital Angular Momentum Quantum Number - *l*

Unlike the Bohr atom, the orbital angular momentum has nothing to do with n. There is a different quantum numbers ℓ that describes the angular momentum. The values of ℓ are:

$$\ell = 0, 1, ..., n - 1$$

It follows from some mathematics that the magnitude of the orbital angular momentum is

$$L = \sqrt{\ell(\ell+1)} \, \frac{h}{2\pi}.$$

We would expect that the energy of the quantum states would depend on this quantum number ℓ . It turns out that it is a unique feature of an inverse square law force that the energy is independent of ℓ .

The Magnetic Quantum Number - m_{ℓ}

It turns out that this magnetic quantum number is related to L_z , the z-component of the angular momentum L.

$$L_z = m_\ell \, \frac{h}{2\pi}$$

The possible values of the magnetic quantum number are.

$$m_{\ell} = -\ell, -\ell + 1, \dots, -2, -1, 0, 1, 2, \dots, \ell - 1, \ell$$

It follows that there are $2\ell + 1$ different m_{ℓ} for each ℓ .

The Spin Quantum Number - m_s

In addition to the orbital angular momentum of the electrons, there is also electron spin. The magnitude of the spin angular momentum happens to be

$$S = \sqrt{\frac{1}{2} \left(\frac{1}{2} + 1\right)} \frac{h}{2\pi}.$$

This spin quantum number is related to S_z , the z-component of the spin angular momentum S.

$$S_z = m_s \frac{h}{2\pi}$$

The possible values of the spin quantum number are.

$$n_s = \pm \frac{1}{2}$$

It follows that there are 2 different m_s states for each set of the other three quantum numbers.

Any quantum state can be labeled by these four numbers: (n, ℓ, m_ℓ, m_s)

Example L.4 - Counting States

How many different quantum states are there for n = 1, for n = 2 and for n = 3.

Solution

For n = 1 we only have $\ell = 0$, and then just $m_{\ell} = 0$. So there are only two states for the two m_s values. Labeling all the (n, ℓ, m_{ℓ}, m_s) gives:

$$\left(1, 0, 0, +\frac{1}{2}\right)$$
 and $\left(1, 0, 0, -\frac{1}{2}\right)$

For n = 2 we only have $\ell = 0$, and then just $m_{\ell} = 0$ and $\ell = 1$ with three different m_{ℓ} values for each. Then for each of the other three sets of quantum numbers there are two spin states, two m_s values. Listing all the (n, ℓ, m_{ℓ}, m_s) values:

$$\left(2, 0, 0, \pm \frac{1}{2}\right),$$

$$\left(2, 1, 1, \pm \frac{1}{2}\right), \left(2, 1, 0, \pm \frac{1}{2}\right), \left(2, 1, -1, \pm \frac{1}{2}\right)$$

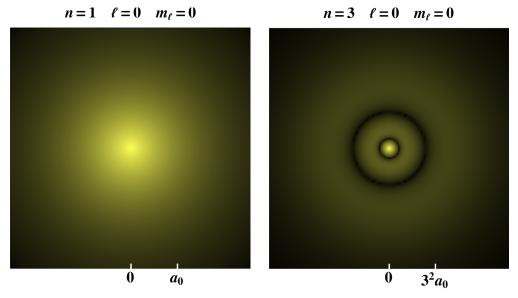
So there are a total of 8 states.

For n = 3 we only have $\ell = 0$, and then just $m_{\ell} = 0$, $\ell = 1$ with three different m_{ℓ} values for each and $\ell = 2$ has five m_{ℓ} values. Listing all the (n, ℓ, m_{ℓ}, m_s) values:

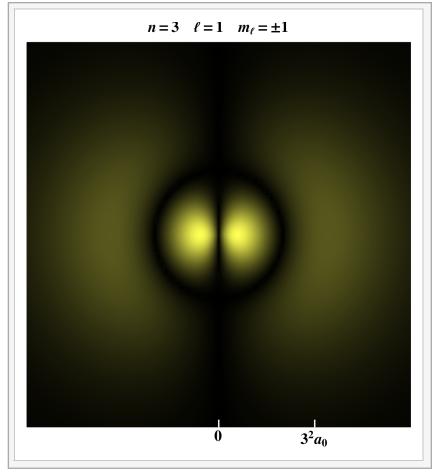
So there are a total of 18 states.

The Electron Probability Clouds

Below is a representation of the probability cloud for the hydrogen ground state on the left and the 3s state on the right. Black denotes zero probabliity.



The probability densities for all states of hydrogen can be seem in the interactive graphic below.



Interactive Figure - Probability densities for all states of the hydrogen atom. (reference)

L.3 - The Periodic Table and Multielectron Atoms

Spectroscopic Notation

We have the same four quantum numbers for multielectron atoms. The number of states and thus the number of possible electrons in a given angular momentum state is $(2 \ell + 1) \times 2$ counting the possible m_{ℓ} values and the two m_s values. There is a standard spectroscopic notation we use to label quantum state. Spectroscopic notation uses a letter for the ℓ values.

ł	0	1	2	3	4
letter	s	р	d	f	g
# of electrons in state	2	6	10	14	18

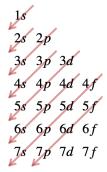
We then write an n = 3, $\ell = 1$ state as 3p. We then use a superscript to represent the number of electrons in a state. If an atom has 2 electrons in this 3p state we write $3p^2$.

The Pauli Principle

In classical physics and in quantum physics, systems tend toward their lowest energy state. For atoms this means the ground state. As temperatures increase a larger fraction of atoms would be excited above their ground state, but at temperatures around room temperature only a small fraction would be excited. That means that in a multielectron atom almost all electrons would fall to the 1*s* state. This does not happen. Electrons, and all spin half particles including protons and neutrons, satisfy the Pauli principle. This means that no two electrons can be in the same quantum state. This has important consequences; it is how the periodic table results from quantum mechanics.

The Periodic Table

The order of the states in terms of increasing energy is by the rule, motivated by some quantum approximations, is that the lower the value of $n + \ell$ has lower energy and for states with the same $n + \ell$ values, the ones with lowest n are lower in energy.



This gives the order of the states: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s. Let us arrange these in a table.

15	1 <i>s</i>		1s							
2s 2p	2 <i>s</i>		2 <i>p</i>							
3s 3p 3d	<u>3s</u>		3 <i>p</i>							
4s 4p 4d 4f	4 <i>s</i>	3 <i>d</i>	4 <i>p</i>							
5s 5p 5d 5f	5 <i>s</i>	4 <i>d</i>	5 <i>p</i>							
6s 6p 6d 6f	6 <i>s</i>	5 <i>d</i>	6 <i>p</i>							
78 7p 7d 7f	7 <i>s</i>	6 <i>d</i>	7 <i>p</i>							
		4 <i>f</i>								
		5f								

Arranging all the elements in this structure gives the usual periodic table.

1 H														2 He			
3 Li	4 Be	of the Elements							5 B	⁶ C	7 N	⁸	9 F	10 Ne			
11	12										13	14	15	16	17	18	
Na	Mg										Al	Si	P	S	CI	Ar	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te		Xe
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Interactive Figure - The Periodic Table - Mouseover gives information about each element.

Electronic Configurations

The electronic configuration of an atom is a listing of (n, ℓ) states with the number of electrons in each state. Hydrogen has one electron in a 1*s* state so we write its electron configuration as $1s^1$. For helium we have 2 electrons in the 1*s* state so we have $1s^2$. For lithium we have the two previous electrons with the third electron in the 2*s* state, so its configuration is $1s^2 2s^1$.

Example L.5 - Electronic Configurations

(a) What is the electronic configuration of carbon, with atomic number Z = 6?

Solution

Just start writing out the states in order with the maximum number of electrons listed until you get more than 6 electrons, then partially populate the highest state.

 $1s^2 2s^2 2p^2$

(b) What is the electronic configuration of sodium, with atomic number Z = 11?

Solution

Do the same thing here. After the 2p state is fully populated there is one electron left for the 3s state.

 $1s^2 2s^2 2p^6 3s^1$

(c) What is the electronic configuration of chlorine, with atomic number Z = 17?

Solution

Do the same thing here. Here the 3p state is one electron short of being fully populated.

$$1s^2 2s^2 2p^6 3s^2 3p^5$$