Atomic Model

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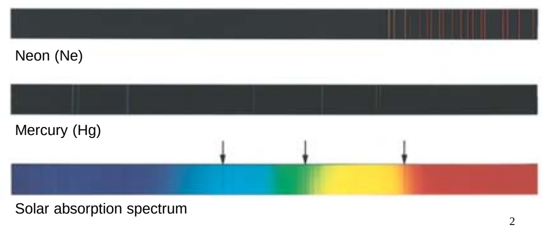
Line Spectra of Atomic Gases

Emission spectra of gases of atoms are composed of discrete lines (i.e., the wavelengths of the emitted light from the atoms are discrete). Why?



2

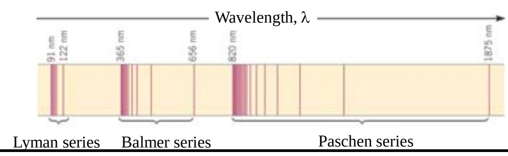
Rydberg's description for the Line Spectrum of Hydrogen

Lyman series $\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$ $n = 2, 3, 4, \ldots$

Balmer series $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ $n = 3, 4, 5, \ldots$

Paschen series $\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$ $n = 4, 5, 6, \ldots$

where $R = 1.097 \times 10^7\ \text{m}^{-1}$ is the Rydberg constant.



Line Spectrum of Hydrogen

By $E = hc/\lambda$, the formulae figured out by Rydberg for λ in the hydrogen spectrum means that the energy of the emitted photons are of the form:

$E = hcR(1/n_2^2 - 1/n_1^2)$, where $n_1 > n_2$ are integers.

If the emissions are due to the hydrogen atoms falling from a higher-energy state to a lower-energy state, it makes sense to think that the energy of a hydrogen atom takes on discrete values equal to hcR/n^2, where n is a number characterizing the energy state of a hydrogen atom. How does this energy quantization ($E \sim 1/n^2$, n=1,2,3,…) dependence come from?

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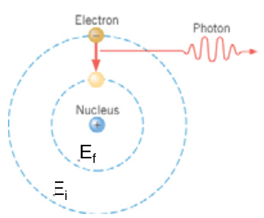
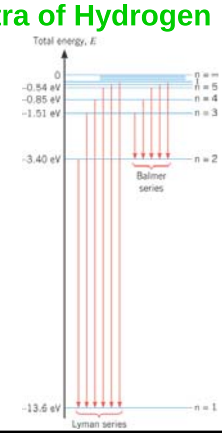
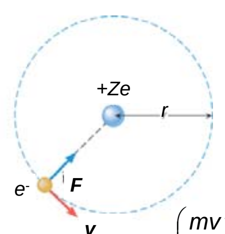
Observed Line Spectra of Hydrogen



$$E_i - E_f = hf$$



Energy of an Atom



$$E = K + U$$

$$= \tfrac{1}{2}mv^2 - \frac{kZe^2}{r}$$

$$E = -\frac{kZe^2}{2r}$$

$$\left(\frac{mv^2}{r} = \frac{kZe^2}{r^2} \Rightarrow mv^2 = \frac{kZe^2}{r}\right)$$

Centripetal force — Electric force

But this doesn't lead to quantization of E. To proceed, we need some hypotheses.

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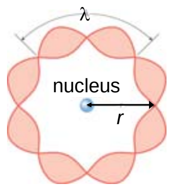
Bohr's Model of Atom

Bohr hypothesized that the angular momentum of electrons in an atom is quantized:

$$mvr_n = \frac{nh}{2\pi} \qquad n = 1, 2, 3, \ldots$$

De Broglie suggested standing particle waves as an explanation for Bohr's angular momentum assumption.

$$2\pi r_n = n\lambda = n\frac{h}{p} = \frac{nh}{mv_n}$$



which leads to Bohr's hypothesis given above.

Bohr's Model for Hydrogen-like Atoms

By using $mvr_n = \frac{nh}{2\pi}$ (p. 7), $mv^2 = \frac{kZe^2}{r}$ and $E = -\frac{kZe^2}{2r}$ (p. 6), Bohr derived an expression for the energy levels of an atom with atomic no. Z:

$$E_n = -\left(\frac{2\pi^2 mk^2e^4}{h^2}\right)\frac{Z^2}{n^2} \qquad n = 1, 2, 3, \ldots$$

$$E_n = -\left(2.18\times10^{-18}\,\text{J}\right)\frac{Z^2}{n^2} \qquad n = 1, 2, 3, \ldots$$

$$= -\left(13.6\,\text{eV}\right)\frac{Z^2}{n^2}$$

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Ionization Energy of Li^{2+}

Li^{2+} is a lithium atom (*Z*=*3*) with only one electron. What is the ionization energy of Li^{2+} in the ground state? (n.b. Ionization energy is the minimum energy required to just free an electron from its atom.)

1. –(13.6 eV)($3^2/1^2$)
2. +(13.6 eV)($3^2/1^2$)
3. -(13.6 eV)($3^2/2^2$)
4. +(13.6 eV)($3^2/2^2$)
5. Cannot be determined

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Ionization Energy of Li^{2+}

Ionization energy is the minimum energy required to just free an electron from its atom. So the final state of the electron should have zero total energy (i.e., K = U = 0.) Thus, the ionization energy is 0 – E_n = -E_n.
Because an Li^{2+} ion has only one orbiting electron, it is like a hydrogen atom with a nuclear charge of +3e. We can use Bohr's model to find the ground state energy, E_1:

$$E_n = -\left(13.6\,\text{eV}\right)\frac{Z^2}{n^2} = -\left(13.6\,\text{eV}\right)\frac{3^2}{1^2} = -122\,\text{eV}$$

$$\text{Ionization energy} = +122\,\text{eV}$$

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Four Quantum Numbers of an Atom

The full quantum mechanical description of atoms actually involves solving the Schrödinger's equation - named after Erwin Schrödinger who shared the Nobel Prize in 1933 for his contribution leading to quantum mechanics. The solution to Schrödinger's equation reveals that four different quantum numbers are required to describe the electronic state of an atom.

1.The principal quantum number *n*.

This number determines the total energy of the atom and can have only integer values. It is the same *n* that appears in Bohr's Energy Levels.

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

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Four Quantum Numbers of an Atom

2. The orbital quantum number ℓ.

$$\ell = 1, 2, 3, \ldots, (n-1)$$

This number determines the orbital angular momentum, *L*, of the electron by:

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

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Four Quantum Numbers of an Atom

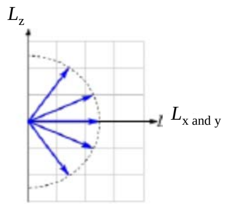
3. The magnetic quantum number m_ℓ

This number characterizes the orientation (or the z component) of the angular momentum vector of the electron.

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

$$m_\ell = -\ell, \ldots -2, -1, 0, 1, 2, \ldots, +\ell$$

Note that there are $2\ell + 1$ values of m_ℓ.



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Four Quantum Numbers of an Atom

4. The spin quantum number m_s

This number is needed because the electron has an intrinsic property called spin.

$$m_s = +\tfrac{1}{2} \text{ or } -\tfrac{1}{2}$$

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Pauli Exclusion Principle

No two electrons can be in the same quantum state. In other words, no two electrons can possess the same set of four quantum numbers.

The consequence of the Pauli Exclusion Principle is that when we fill the energy levels of an atom with electrons (where there are Z of them), we can only fill one electron in each distinguishable slot (i.e., sub-orbital and spin state) available in a energy level at a time, from low to high energies.

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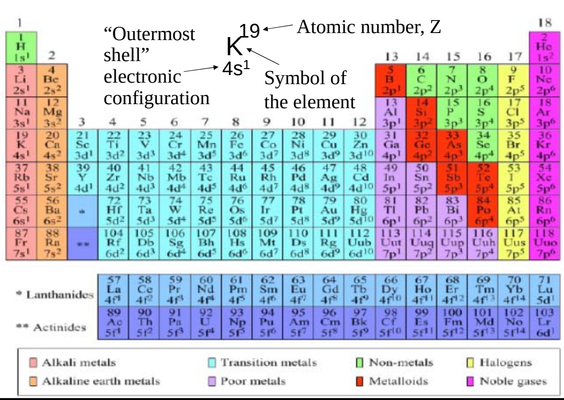
Number-letter-number notation for electronic configuration of atoms

$4d^5$

- The value of *n*. (the 4)
- A letter representing the value of ℓ (see table below) (the d)
- The number of filled electron states for the l orbital. The maximum of this number is $2(2\ell + 1)$ (the 5)
  - 2: Spin degrees of freedom
  - $(2\ell + 1)$: Degrees of freedom associated with L_z

Value of ℓ	0	1	2	3	4	5	6
Letter	*s*	*p*	*d*	*f*	*g*	*h*	*i*

Periodic Table of Elements



Filling the electrons – Shell Model

The no. of electrons an atom possesses is Z. By filling the electrons of an atom according to the Shell Model, which is based on the four quantum numbers, we can understand the chemical properties of the elements as grouped in the periodic table. From the periodic table, the chemical property of an atom is largely determined by its "outermost shell" electrons.

Shell no. (n)								Max. no. of e^-
1	$1s^2$							2
2	$2s^2$	$2p^6$						8
3	$3s^2$	$3p^6$	$3d^{10}$					18
4	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$				32
5	$5s^2$	$5p^6$	$5d^{10}$	$5f^{14}$	$5g^{18}$			50
6	$6s^2$	$6p^6$	$6d^{10}$	$6f^{14}$	$6g^{18}$	$6h^{22}$		72
7	$7s^2$	$7p^6$	$7d^{10}$	$7f^{14}$	$7g^{18}$	$7h^{22}$	$7i^{26}$	98

Filling the electrons – Shell Model

The table shows some examples of electronic configurations of elements successfully predicted by the Shell Model.

These are what would give the lowest possible energy the atoms can have and so is called the **ground-state**. If the electronic configuration of an atom deviates from that of the ground-state, the atom is in an **excited state**. De-excitation of an atom leads to emissions.

Element	Number of Electrons	Configuration of the Electrons
Hydrogen (H)	1	$1s^1$
Helium (He)	2	$1s^2$
Lithium (Li)	3	$1s^2\ 2s^1$
Beryllium (Be)	4	$1s^2\ 2s^2$
Boron (B)	5	$1s^2\ 2s^2\ 2p^1$
Carbon (C)	6	$1s^2\ 2s^2\ 2p^2$
Nitrogen (N)	7	$1s^2\ 2s^2\ 2p^3$
Oxygen (O)	8	$1s^2\ 2s^2\ 2p^4$
Fluorine (F)	9	$1s^2\ 2s^2\ 2p^5$
Neon (Ne)	10	$1s^2\ 2s^2\ 2p^6$
Sodium (Na)	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Magnesium (Mg)	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$
Aluminum (Al)	13	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$