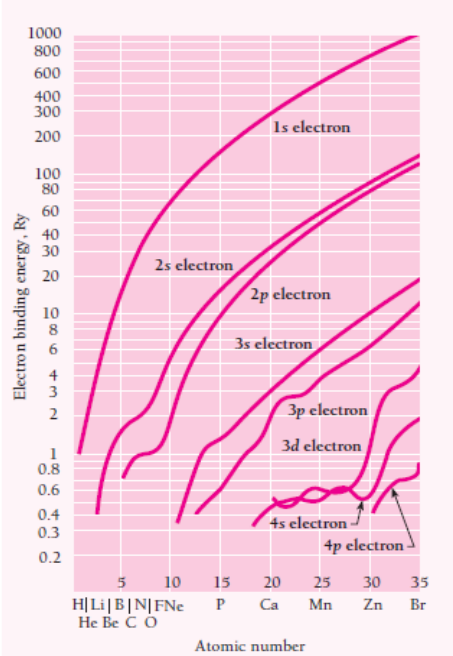
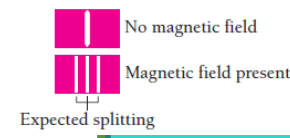
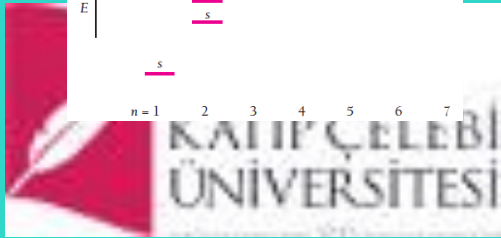
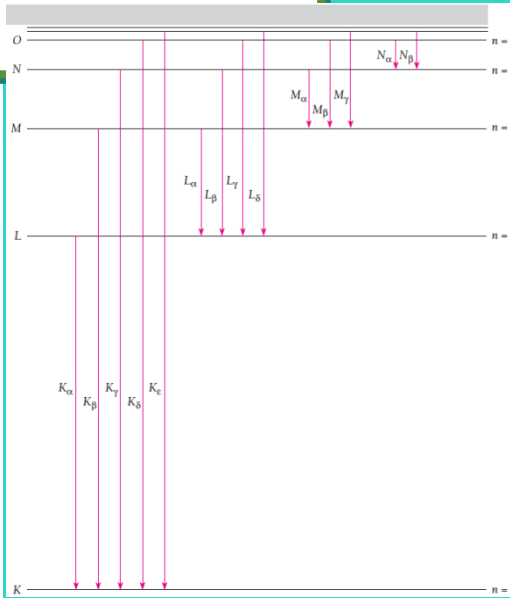


Chapter 7

Many-Electron Atoms



n	l	Subshell	Capacity 2(2l+1)
1	0	1s	2
2	0	2s	2
2	1	2p	6
3	0	3s	2
3	1	3p	6
4	0	4s	2
3	2	3d	10
4	1	4p	6
5	0	5s	2
4	2	4d	10
4	3	4f	14
5	2	5d	10
6	1	6p	6
7	0	7s	2
5	3	5f	14
6	2	6d	10



- | | | | |
|------------|--|------------------|--|
| 7.1 | ELECTRON SPIN
<i>Round and round it goes forever</i> | 7.6 | EXPLAINING THE PERIODIC TABLE
<i>How an atom's electron structure determines its chemical behavior</i> |
| 7.2 | EXCLUSION PRINCIPLE
<i>A different set of quantum numbers for each electron in an atom</i> | 7.7 | SPIN-ORBIT COUPLING
<i>Angular momenta linked magnetically</i> |
| 7.3 | SYMMETRIC AND ANTISYMMETRIC WAVE FUNCTIONS
<i>Fermions and bosons</i> | 7.8 | TOTAL ANGULAR MOMENTUM
<i>Both magnitude and direction are quantized</i> |
| 7.4 | PERIODIC TABLE
<i>Organizing the elements</i> | 7.9 | X-RAY SPECTRA
<i>They arise from transitions to inner shells</i> |
| 7.5 | ATOMIC STRUCTURES
<i>Shells and subshells of electrons</i> | APPENDIX: | ATOMIC SPECTRA |

- Quantum mechanics explains certain properties of the hydrogen atom in an accurate, straightforward, and beautiful way.
- However, it cannot approach a complete description of this atom or of any other without taking into account electron spin and the exclusion principle.
- Many spectral lines actually consist of two separate lines that are very close together.
 - An example of this **fine structure** (electron spin and relativistic corrections): first line of the Balmer series of hydrogen, theoretical prediction is for a single line of wavelength 656.3 nm while in reality there are two lines 0.14 nm apart.
 - Another failure occurs in the (normal) Zeeman effect that the spectral lines of an atom in a magnetic field should each be split into the three components.
- ***Round and round it goes forever.*** two Dutch graduate students, Samuel Goudsmit and George Uhlenbeck, proposed in 1925 that

Every electron has an intrinsic angular momentum, called spin. Associated with this angular momentum is a magnetic moment.

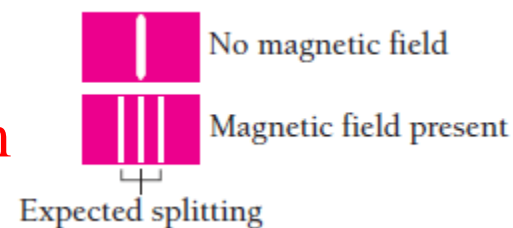


Figure 7.1 The normal Zeeman effect.

- Classical picture of an electron as a *charged sphere spinning* on its axis.
 - The rotation involves angular momentum, and because the electron is negatively charged, it has a magnetic moment μ_s opposite in direction to its angular momentum vector \mathbf{S} .
 - Serious objection: observations of the scattering of electrons by other electrons indicate that the electron must be less than 10^{-16} m across, and quite possibly is a point particle. In order to have the observed angular momentum associated with electron spin, so small an object would have to rotate with an equatorial velocity many times greater than the velocity of light!
- In 1929 the fundamental nature of electron spin was confirmed by Paul Dirac's development of relativistic quantum mechanics. He found that a particle with the mass and charge of the electron *must* have the intrinsic angular momentum and magnetic moment proposed for the electron by Goudsmit and Uhlenbeck.



Paul Adrien
Maurice Dirac
(1902–1984)
Nobel Prize in
Physics in 1933

The quantum number s describes the spin angular momentum of the electron. The only value s can have is $s = 1/2$, which follows both from Dirac's theory and from spectral data. The magnitude S of the angular momentum due to electron spin is given in terms of the spin quantum number s by

$$S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar \quad (\text{Spin angular momentum})$$

Example 7.1

Find the equatorial velocity of an electron under the assumption that it is a uniform sphere of radius $r=5.00 \times 10^{-17}$ m that is rotating about an axis through its center.

Solution

The angular momentum of a spinning sphere is $I\omega$, where $I = \frac{2}{5} mr^2$ is its moment of inertia and $\omega = v/r$ is its angular velocity. From Eq. (7.1) the spin angular momentum of an electron is $S = (\sqrt{3}/2)\hbar$, so

$$S = \frac{\sqrt{3}}{2} \hbar = I\omega = \left(\frac{2}{5} mr^2 \right) \left(\frac{v}{r} \right) = \frac{2}{5} mvr$$

$$v = \left(\frac{5\sqrt{3}}{4} \right) \frac{\hbar}{mr} = \frac{(5\sqrt{3})(1.055 \times 10^{-34} \text{ J} \cdot \text{s})}{(4)(9.11 \times 10^{-31} \text{ kg})(5.00 \times 10^{-17} \text{ m})} = 5.01 \times 10^{12} \text{ m/s} = 1.67 \times 10^4 c$$

The equatorial velocity of an electron on the basis of this model must be over 10,000 times the velocity of light, which is impossible. No classical model of the electron can overcome this difficulty.

- The **space quantization** of electron spin is described by the spin magnetic quantum number m_s .
 - Spin angular-momentum vector can have the $2s + 1 = 2$ orientations specified by $m_s = +1/2$ (“spin up”) and $m_s = -1/2$ (“spin down”), as in Fig. 7.2.
 - The component S_z of the spin angular momentum of an electron along a magnetic field in the z direction is determined by the spin magnetic quantum number, so that $S_z = m_s \hbar = \pm \frac{1}{2} \hbar$ (z component of spin angular momentum)
- The gyromagnetic ratio for electron orbital motion is $-e/2m$. The gyromagnetic ratio characteristic of electron spin is almost exactly twice.
- Spin magnetic moment μ_s of an electron is related to its spin angular momentum \mathbf{S} by $\mu_s = -\frac{e}{m} \mathbf{S}$ (Spin magnetic moment)

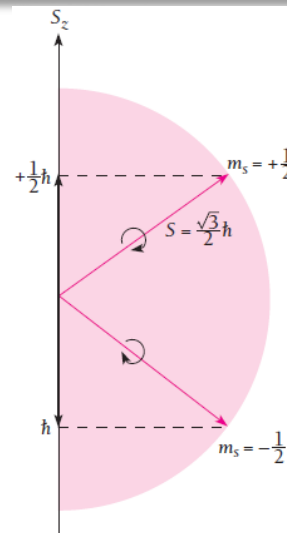


Figure 7.2 The two possible orientations of the spin angular momentum vector are “spin up” ($m_s = +1/2$) and “spin down” ($m_s = -1/2$).

The possible components of μ_s along any axis, say the z axis, are therefore limited to $\mu_{sz} = \pm \frac{e\hbar}{2m} = \pm \mu_B$ (z component of spin magnetic moment) where μ_B is the Bohr magneton ($9.274 \times 10^{-24} \text{ J/T} = 5.788 \times 10^{-5} \text{ eV/T}$).

The introduction of electron spin into the theory of the atom means that a total of four quantum numbers, n , l , m_l , and m_s , is needed to describe each possible state of an atomic electron. These are listed in Table 7.1.

Table 7.1 Quantum Numbers of an Atomic Electron

Name	Symbol	Possible Values	Quantity Determined
Principal	n	1, 2, 3, . . .	Electron energy
Orbital	l	0, 1, 2, . . . , $n - 1$	Orbital angular-momentum magnitude
Magnetic	m_l	$-l, . . . , 0, . . . , +l$	Orbital angular-momentum direction
Spin magnetic	m_s	$-\frac{1}{2}, +\frac{1}{2}$	Electron spin direction

- A different set of quantum numbers for each electron in an atom.
- In a normal hydrogen atom, the electron is in its quantum state of lowest energy.
 - What about more complex atoms? Are all 92 electrons of a uranium atom in the same quantum state, jammed into a single probability cloud?
 - An example is the great difference in chemical behavior shown by certain elements whose atomic structures differ by only one electron. Thus the elements that have the atomic numbers 9, 10, and 11 are respectively the chemically active halogen gas fluorine, the inert gas neon, and the alkali metal sodium.



Wolfgang Pauli
(1900–1958)
Nobel Prize in
Physics in 1945

Since the **electron structure** of an atom controls how it interacts with other atoms, it makes no sense that the chemical properties of the elements should change so sharply with a small change in atomic number if all the electrons in an atom were in the same quantum state.

- In 1925 Wolfgang Pauli discovered the fundamental principle that governs the electronic configurations of atoms having more than one electron. His **exclusion principle** states that **No two electrons in an atom can exist in the same quantum state. Each electron must have a different set of quantum numbers n, l, m_l, m_s .**

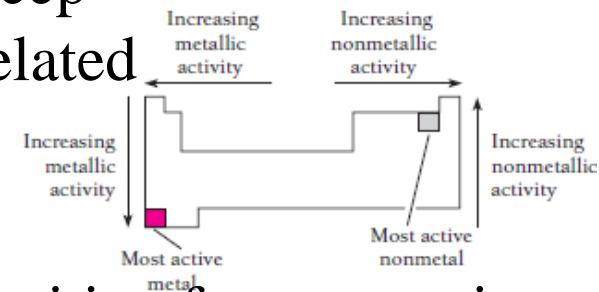


Dimitri
Mendeleyev
(1834-1907)

- *Organizing the elements*
- In 1869 the Russian chemist Dmitri Mendeleev formulated:
When the elements are listed in order of atomic number, elements with similar chemical and physical properties recur at regular intervals
- Elements with similar properties form the **groups** shown as vertical columns.
 - Group 1 consists of hydrogen plus the alkali metals, which are all *soft, have low melting points, and are very active chemically*.
 - Hydrogen, although physically a nonmetal, behaves chemically much like an active metal.
 - Group 7 consists of the halogens, *volatile non-metals that form diatomic molecules in the gaseous state*.
 - Like the alkali metals, the halogens are chemically active, but as oxidizing agents rather than as reducing agents.
 - Group 8 consists of the inert gases. As their name suggests, they are *inactive chemically*: they form virtually no compounds with other elements, and their atoms *do not join together into molecules*.

- The horizontal rows are called **periods**.
- The first three periods are broken in order to keep their members aligned with the most closely related elements of the long periods below.
- **Most of the elements are metals.**
 - Across each period is a more or less steady transition from an active metal through less active metals and weakly active nonmetals to highly active nonmetals and finally to an inert gas.
- A series of **transition elements** appears in each period after the third between the group 2 and group 3 elements.
 - *The transition elements are metals, in general hard and brittle with high melting points, that have similar chemical behavior.*
 - Fifteen of the transition elements in period 6 are virtually indistinguishable in their properties and are known as the **lanthanide elements** (or **rare earths**).
 - Another group of closely related metals, the **actinide** elements, is found in period 7.

Figure 7.6 How chemical activity varies in the periodic table.



7.4 Periodic Table

Table 7.2

The Periodic Table of the Elements

Group	1	2	Transition metals										3	4	5	6	7	8									
Period 1	1 H Hydrogen 1.008		<p>The number above the symbol of each element is its atomic number, and the number below its name is its average atomic mass. The elements whose atomic masses are given in parentheses do not occur in nature but have been created in nuclear reactions. The atomic mass in such a case is the mass number of the most long-lived radioisotope of the element.</p> <p>Elements with atomic numbers 110, 111, 112, 114, and 116 have also been created but not yet named.</p>																			2 He Helium 4.003					
2	3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18									
3	11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminium 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95									
4	19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.8	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.59	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80									
5	37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.1	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.9	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.8									
6	55 Cs Cesium 132.9	56 Ba Barium 137.3											72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.9	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
7	87 Fr Francium (223)	88 Ra Radium 226.0											104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Ns Nielsbohrium (262)	108 Hs Hassium (264)	109 Mt Meitnerium (266)	Halogens Inert gases								
Alkali metals			Lanthanides (rare earths)																								
			57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0										
			89 Ac Actinium (227)	90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (260)	102 No Nobelium (259)	103 Lw Lawrencium (262)	Actinides									

- *Shells and subshells of electrons*
- Two basic principles determine the structures of atoms with more than one electron:
 1. A system of particles is **stable** when its total energy is a minimum.
 2. Only one electron can exist in any particular quantum state in an atom.
- While the various electrons in a complex atom certainly interact directly with one another, much about atomic structure can be understood by simply considering each electron as though it exists in a constant mean electric field.
 - Nuclear charge Ze decreased by the partial shielding of those other electrons that are closer to the nucleus.
- Electrons that have the same principal quantum number n (same atomic **shell**) therefore interact with roughly the same electric field and have similar energies.

$n =$	1	2	3	4	5	...	
	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>	<i>O</i>	...	(7.13 Atomic shells)
- The energy of an electron in a particular shell also on its orbital quantum number l , though not as much as on n .

- In a complex atom the degree to which the full nuclear charge is shielded from a given electron by intervening shells of other electrons varies with its probability-density distribution.
- An electron of small l is more likely to be found near the nucleus where it is poorly shielded by the other electrons than is one of higher l (see Fig. 6.11).
- The result is a lower total energy (that is, higher binding energy) for the electron.
- The electrons in each shell accordingly increase in energy with increasing l (see Fig. 7.8).
- Electrons that share a certain value of l in a shell are said to occupy the same **subshell**.
 - All the electrons in a subshell have almost identical energies, since the dependence of electron energy upon m_l and m_s is comparatively minor.

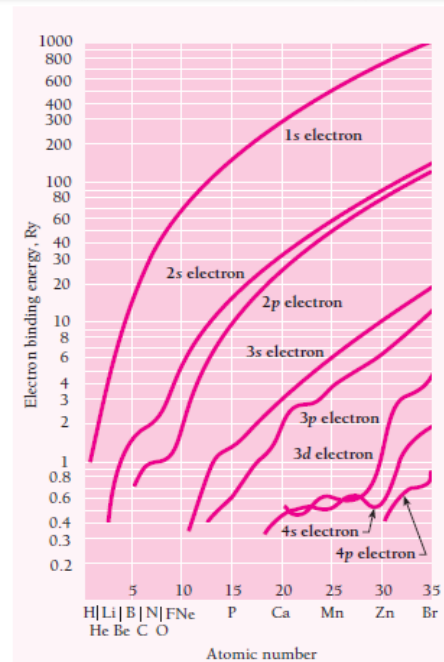


Figure 7.8 The binding energies of atomic electrons in rydbergs. (1 Ry=13.6 eV ground-state energy of H atom.)

- *How an atom's electron structure determines its chemical behavior.*
- An atomic shell or subshell that contains its full quota of electrons is said to **be closed**.
- *The total orbital and spin angular momenta of the electrons in a closed subshell are zero, and their effective charge distributions are perfectly symmetrical.*

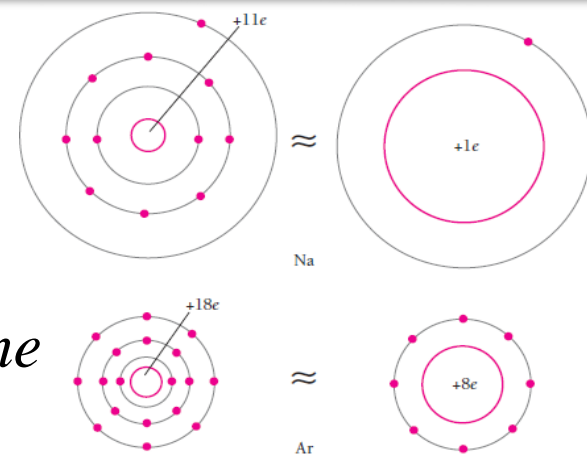


Figure 7.9 Schematic representation of electron shielding in the sodium and argon atoms.

- The electrons in a closed shell are all very tightly bound, since the positive nuclear charge is large relative to the negative charge of the inner shielding electrons (see Fig. 7.9).
- Because an atom with only closed shells has no dipole moment, it does not attract other electrons, and its electrons cannot be easily detached. We expect such atoms to be passive chemically, like the inert gases.

- An atom of any of the alkali metals of group 1 has a single s electron in its outer shell.
 - Such an electron is relatively far from the nucleus.
 - It is also shielded by the inner electrons from all but an effective nuclear charge of approximately $+e$ rather than $+Ze$.
 - Relatively little work is needed to detach an electron from such an atom, and the alkali metals accordingly form positive ions of charge $+e$ readily.

Example 7.2

The ionization energy of lithium is 5.39 eV. Use this figure to find the effective charge that acts on the outer (2s) electron of the lithium atom.

Solution

If the effective nuclear charge is Ze instead of e , Eq. (4.15) becomes

$$E_n = \frac{Z^2 E_1}{n^2}$$

Here $n = 2$ for the 2s electron, its ionization energy is $E_2 = -5.39$ eV, and $E_1 = -13.6$ eV is the ionization energy of the hydrogen atom. Hence

$$Z = n \sqrt{\frac{E_2}{E_1}} = 2 \sqrt{\frac{5.39 \text{ eV}}{13.6 \text{ eV}}} = 1.26$$

The effective charge is $1.26e$ and not e because the shielding of $2e$ of the nuclear charge of $3e$ by the two 1s electrons is not complete: as we can see in Fig. 6.11, the 2s electron has a certain probability of being found inside the 1s electrons.

7.6 Explaining the Periodic Table: Ionization Energy

- Inert gases have the highest ionization energies and the alkali metals the lowest.
- *The larger an atom, the farther the outer electron is from the nucleus and the weaker the force is that holds it to the atom.*
- This is why the ionization energy generally decreases as we go down a group in the periodic table.
- The increase in ionization energy from left to right across any period is accounted for by the increase in nuclear charge while the number of inner shielding electrons stays constant.
- At the other extreme from alkali metal atoms are halogen atoms, whose imperfectly shielded nuclear charges tend to complete their outer subshells by picking up an additional electron each.

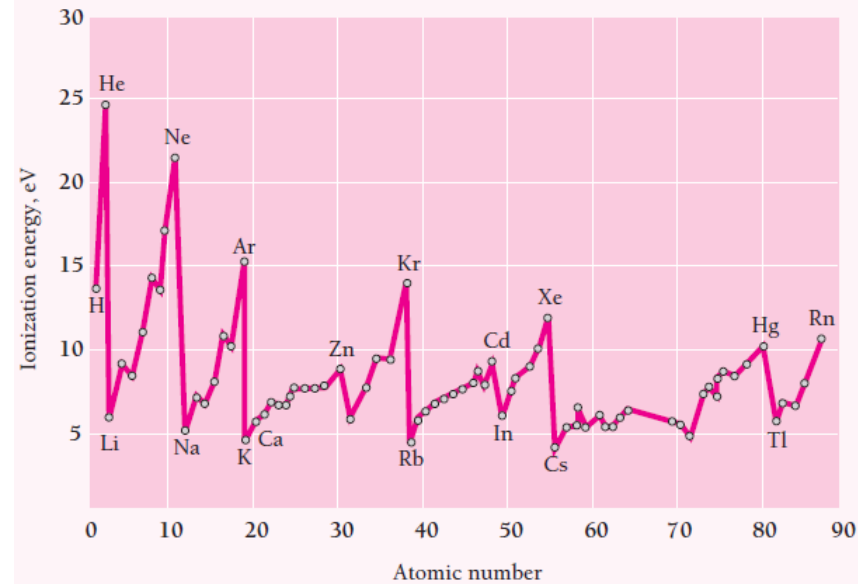


Figure 7.10 Variation of ionization energy with atomic number.

- The periodicity in Fig. 7.11 has a *similar origin in the partial shielding by inner electrons of the full nuclear charge.*
- The greater the shielding, the lower the binding energy of an outer electron and the farther it is on the average from the nucleus.
- The relatively small range of atomic radii is not surprising in view of the binding-energy curves of Fig. 7.8.
- In contrast to the enormous increase in the binding energies of the unshielded 1s electrons with Z , the binding energies of the outermost electrons (whose probability-density distributions are what determine atomic size) vary through a narrow range.
 - The heaviest atoms, with over 90 electrons, have radii only about 3 times that of the hydrogen atom, and even the cesium atom, the largest in size, has a radius only 4.4 times that of the hydrogen atom.

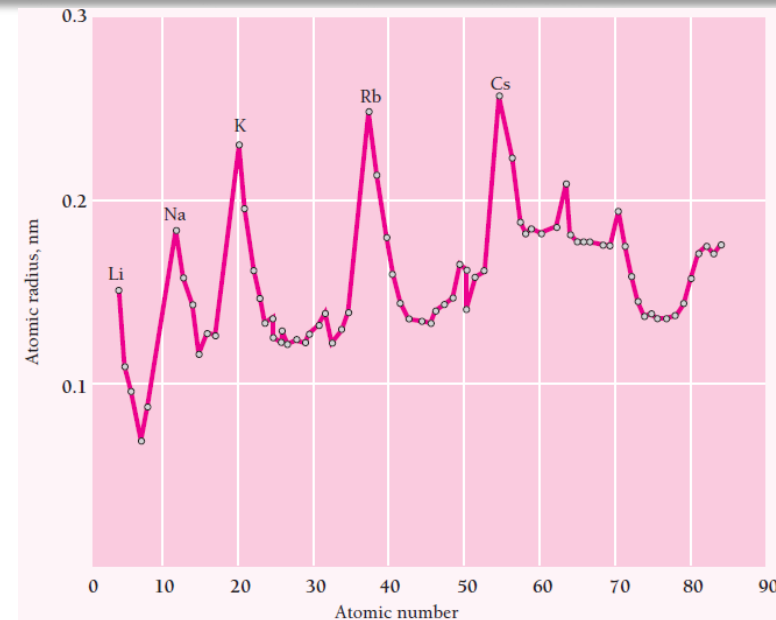


Figure 7.11 Atomic radii of the elements.

- The origin of the transition elements lies in the tighter binding of s electrons than d or f electrons in complex atoms.
- The first element to exhibit this effect is potassium, whose outermost electron is in a $4s$ instead of a $3d$ substate.
- The difference in binding energy between $3d$ and $4s$ electrons is not very great, as the configurations of chromium and copper show.



Figure 7.12 The sequence of quantum states in an atom. Not to scale.

- In both these elements an additional $3d$ electron is present at the expense of a vacancy in the $4s$ subshell.
- The order in which electron subshells tend to be filled, together with the maximum occupancy of each subshell, is usually as follows:

$$1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^{10} \ 4p^6 \ 5s^2$$

$$4d^{10} \ 5p^6 \ 6s^2 \ 4f^{14} \ 5d^{10} \ 6p^6 \ 7s^2 \ 6d^{10} \ 5f^{14}$$

n	l	Subshell	Capacity $2(2l+1)$
1	0	1s	2
2	0	2s	2
2	1	2p	6
3	0	3s	2
3	1	3p	6
4	0	4s	2
3	2	3d	10
4	1	4p	6
5	0	5s	2
4	2	4d	10
5	1	5p	6
6	0	6s	2
4	3	4f	14
5	2	5d	10
6	1	6p	6
7	0	7s	2
5	3	5f	14
6	2	6d	10

Figure 7.12 illustrates this sequence.

- The remarkable similarities in chemical behavior among the lanthanides and actinides are easy to understand on the basis of this sequence.
 - All the lanthanides have the same $5s^25p^66s^2$ configurations but have incomplete $4f$ subshells. The addition of $4f$ electrons has almost no effect on the chemical properties of the lanthanide elements, which are determined by the outer electrons.
 - Similarly, all the actinides have $6s^26p^67s^2$ configurations and differ only in the numbers of their $5f$ and $6d$ electrons.
 - These irregularities in the binding energies of atomic electrons are also responsible for the lack of completely full outer shells in the heavier inert gases.

- In general, the electrons in a subshell remain **unpaired**-that is, have parallel spins-whenver possible (see Table 7.5).

Table 7.5 Electron Configurations of Elements from $Z=5$ to $Z=10$. The p electrons have parallel spins whenever possible, in accord with Hund's rule.

Element	Atomic Number	Configuration	Spins of p Electrons		
Boron	5	$1s^2 2s^2 2p^1$	↑		
Carbon	6	$1s^2 2s^2 2p^2$	↑	↑	
Nitrogen	7	$1s^2 2s^2 2p^3$	↑	↑	↑
Oxygen	8	$1s^2 2s^2 2p^4$	↑↓	↑	↑
Fluorine	9	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑
Neon	10	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓

- This principal is called *Hund's rule*.
- The ferromagnetism of iron, cobalt, and nickle ($Z=26, 27, 28$) is in part a consequence of Hund's rule.
- The $3d$ subshells of their atoms are only *partially occupied*, and the electrons in these subshells do not pair off to permit their spin magnetic moments to cancel out.
- In iron, for instance, five of the six $3d$ electrons have parallel spins, so that each iron atom has a large resultant magnetic moment.

- The origin of Hund's rule lies in the mutual repulsion of atomic electrons.
- Because of this repulsion, the farther apart the electrons in an atom are, the lower the energy of the atom.
- Electrons in the same subshell with the same spin must have different m_l values and accordingly are described by wave functions whose spatial distributions are different.
- *Electrons with parallel spins are therefore more separated in space than they would be if they paired off.*
- **This arrangement, having less energy, is the more stable one.**

- *They arise from transitions to inner shells.*
- We learned that the x-ray spectra of targets bombarded by fast electrons show narrow spikes at wavelengths characteristic of the target material.
- The line spectrum comes from electronic transitions within atoms that have been disturbed *by the incident electrons*.
- The transitions of the outer electrons of an atom usually involve only a few electronvolts of energy, and even removing an outer electron requires at most 24.6 eV (for helium) (in or near the visible part).
- The inner electrons of heavier elements are a quite different matter, because these electrons are *not well shielded* from the full nuclear charge by intervening electron shells and so are very tightly bound.
 - In sodium, for example, only 5.13 eV is needed to remove the outermost 3s electron, whereas the corresponding figures for the inner ones are 31 eV for each 2p electron, 63 eV for each 2s electron, and 1041 eV for each 1s electron.
- *Transitions that involve the inner electrons in an atom are what give rise to x-ray line spectra because of the high photon energies involved.*

Figure 7.20 shows the energy levels (not to scale) of a heavy atom.

- Let us look at what happens when an energetic electron strikes the atom and knocks out one of the K -shell electrons.
- An atom with a missing K electron gives up most of its considerable excitation energy in the form of an x-ray photon when an electron from an outer shell drops into the “hole” in the K shell.
- As indicated in Fig. 7.20, the **K series** of lines in the x-ray spectrum of an element consists of wavelengths arising in transitions from the L, M, N, \dots levels to the K level.
- It is easy to find an approximate relationship between the frequency of the K_{α} x-ray line of an element and its atomic number Z .

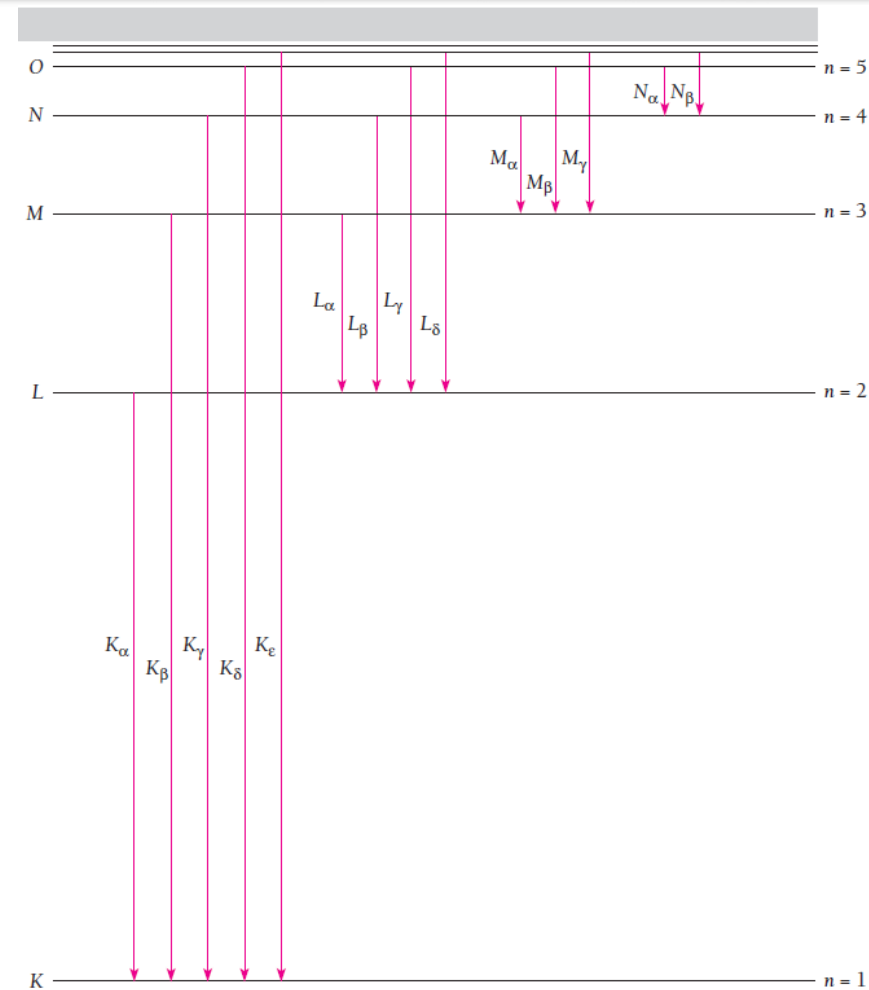


Figure 7.20 The origin of x-ray spectra.

- K_α photon is emitted when an L ($n = 2$) electron undergoes a transition to a vacant K ($n = 1$) state.
- The L electron experiences a nuclear charge of Ze that is reduced to an effective charge in the neighborhood of $(Z - 1)e$ by the shielding effect of the remaining K electron. Thus

$$\nu = \frac{m(Z - 1)^2 e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = cR(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$\nu = \frac{3cR(Z - 1)^2}{4} \quad (7.21 \text{ } K_\alpha \text{ x-rays})$$

- The energy of a K_α x-ray photon is given in electronvolts in terms of $(Z - 1)$ by the formula

$$E(K_\alpha) = (10.2 \text{ eV})(Z - 1)^2 \quad (7.22)$$
- In the operation of this x-ray spectrometer, a stream of fast electrons is directed at a sample of unknown composition.
- Some of the electrons knock out inner electrons in the target atoms, and when outer electrons replace them, x-ray are emitted whose wavelengths are characteristic of the elements present.
- *The identity and relative amounts of the elements in the sample can be found in this way.*

Example 7.3

Which element has a K_{α} x-ray line whose wavelength is 0.180 nm?

Solution

The frequency corresponding to a wavelength of 0.180 nm = 1.80×10^{-10} m is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.80 \times 10^{-10} \text{ m}} = 1.67 \times 10^{18} \text{ Hz}$$

From Eq. (7.21) we have

$$Z - 1 = \sqrt{\frac{4}{3cR}} = \sqrt{\frac{(4)(1.67 \times 10^{18} \text{ Hz})}{(3)(3.00 \times 10^8 \text{ m/s})(1.097 \times 10^7 \text{ m}^{-1})}} = 26$$
$$Z = 27$$

The element with atomic number 27 is cobalt.

- An atom with a missing inner electron can also lose excitation energy by the **Auger effect** without emitting an x-ray photon.
- In this effect, an outer-shell electron is ejected from the atom at the same time that another outer-shell electron drops to the incomplete inner shell.
- Thus the ejected electron carries off the atom's excitation energy instead of a photon doing this (see Fig. 7.21).
- In a sense the Auger effect represents an internal photoelectric effect, although the photon never actually comes into being within the atom.
- *The Auger process is competitive with x-ray emission in most atoms, but the resulting electrons are usually absorbed in the target material while the x-rays emerge to be detected.*
- Those Auger electrons that do emerge come either from atoms on the surface of the material or just below the surface.
- Because the energy levels of an atom are affected by its participation in a chemical bond, the energies of Auger electrons provide insight into the chemical environment of the atoms involved.

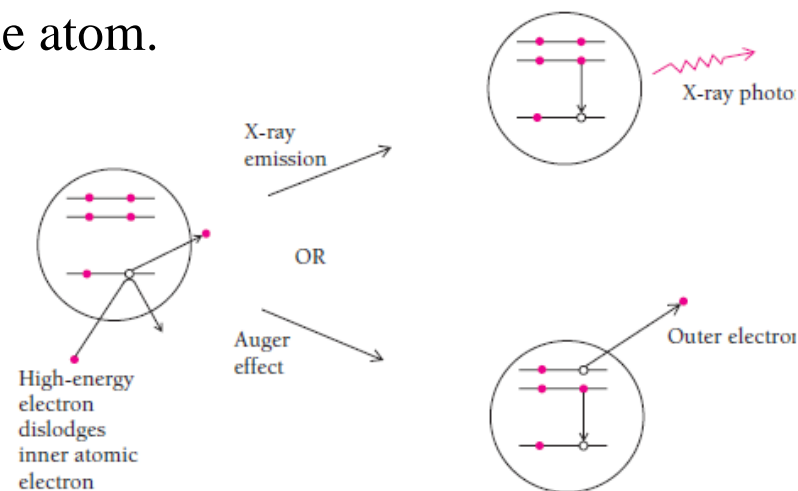


Figure 7.21 When an electron from an outer shell of an atom with a missing inner electron drops to fill the vacant state, the excitation energy can be carried off by an x-ray photon or by another outer electron. The latter process is called the Auger effect.

1. (a) How many different sets of quantum numbers (n, l, m_l, m_s) are possible for an electron in the 4f level? (b) Suppose a certain atom has three electrons in the 4f level. What is the maximum possible value of the total m_s of the three electrons? (c) What is the maximum possible total m_l of three 4f electrons? (d) Suppose an atom has ten electrons in the 4f level. What is the maximum possible value of the total m_s of the ten 4f electrons? (e) What is the maximum possible total m_l of ten 4f electrons?

a) $4f \rightarrow n=4, l=3 \rightarrow m_l = +3, +2, +1, 0, -1, -2, -3$ & $m_s = +\frac{1}{2}, -\frac{1}{2} \Rightarrow 7 \times 2 = \boxed{14}$
 7 possible combinations

b) Three $e_s \rightarrow 7 e_s$ can have state $m_s = +\frac{1}{2} \Rightarrow$ three e_s $m_s = 3 \times +\frac{1}{2} = \boxed{+\frac{3}{2}}$

c) $m_l = +3 \rightarrow m_s = +\frac{1}{2}$ & $m_l = +2 \rightarrow m_s = +\frac{1}{2} \Rightarrow 2 \times (+3) + 1 \times (+2) = \boxed{+8}$
 $m_s = -\frac{1}{2}$

d) Ten $e_s \rightarrow 7 e_s$ can have state $m_s = +\frac{1}{2}$ & 3 e_s can have state $m_s = -\frac{1}{2}$
 $\Rightarrow 7 \times (+\frac{1}{2}) + 3 \times (-\frac{1}{2}) = \boxed{2}$

e) $m_l = +3 \rightarrow m_s = +\frac{1}{2}$ & $m_l = +2 \rightarrow m_s = +\frac{1}{2}$ & $m_l = +1 \rightarrow m_s = +\frac{1}{2}$ & $m_l = 0 \rightarrow m_s = +\frac{1}{2}$ & $m_l = -1 \rightarrow m_s = +\frac{1}{2}$
 $m_s = -\frac{1}{2}$ & $m_s = -\frac{1}{2}$ & $m_s = -\frac{1}{2}$
 $10 e_s = 2 + 2 + 2 + 2 + 2$
 $\Rightarrow 2 \times (+3) + 2 \times (+2) + 2 \times (+1) + 2 \times (0) + 2 \times (-1) = \boxed{10}$

2. Copper has the electronic configuration $[\text{Ar}]4s^13d^{10}$ in its ground state. By adding a small amount of energy (about 1 eV) to a copper atom, it is possible to move one of the $3d$ electrons to the $4s$ level and change the configuration to $[\text{Ar}]4s^23d^9$. By adding still more energy (about 5 eV), one of the $3d$ electrons can be moved to the $4p$ level so that the configuration becomes $[\text{Ar}]4s^13d^94p^1$. For each of these configurations, determine the maximum value of the total m_s of the electrons.

Copper $\rightarrow [\text{Ar}]4s^13d^{10}$: ground state \rightarrow single $4s$ e^- contributes to m_s : $+1/2$
 adding 1eV $\rightarrow [\text{Ar}]4s^23d^9$ ① $3d^{10}$: filled subshell has equal numbers of e^- in $m_s = \pm 1/2$ states. \rightarrow at total 0.
 adding more 5eV $\rightarrow [\text{Ar}]4s^13d^94p^1$ ②

① 2 $4s$ $e^-s \rightarrow 0$
 9 $3d$ $e^-s \rightarrow 5 \times (+1/2) + 4 \times (-1/2) = +1/2$

② 1 $4s$ $e^- \rightarrow +1/2$
 9 $3d$ $e^-s \rightarrow +1/2$
 1 $4p$ $e^- \rightarrow +1/2$ } so at maximum $m_s = +3/2$

3. (a) The ionization energy of sodium is 5.14 eV. What is the effective charge seen by the outer electron? (b) If the 3s electron of a sodium atom is moved to the 4f state, the measured binding energy is 0.85 eV. What is the effective charge seen by an electron in this state?

$$E_n = Z_{\text{eff}}^2 \frac{E_1}{n^2}, \text{ where } E_1 = -13.6 \text{ eV}$$

$$a) 3s, E_3 = -5.14 \text{ eV} \rightarrow Z_{\text{eff}} = n \sqrt{\frac{E_3}{-13.6 \text{ eV}}} = 3 \sqrt{\frac{-5.14 \text{ eV}}{-13.6 \text{ eV}}} = \boxed{1.84}$$

Na: $1s^2 2s^2 2p^6 3s^1$, 11(+e) in nucleus } $1 = Z_{\text{eff}}$ = expected
 10(-e) in core e_s

So, less screened by the inner e_s . 3s electron is penetrating the inner orbit.

$$b) 4f, E_4 = -0.85 \text{ eV} \rightarrow Z_{\text{eff}} = 4 \sqrt{\frac{-0.85 \text{ eV}}{-13.6 \text{ eV}}} = \boxed{1.00}$$

so, screening is complete.

4. Use Hund's rules to find the ground-state quantum numbers of nitrogen.

Nitrogen: $1s^2 2s^2 2p^3$, Quantum numbers: n, l, m_l, m_s , Ground state
 $2p^3$: 3 e^- to have $m_s = +1/2 \rightarrow m_s = +3/2 \Leftrightarrow \uparrow \uparrow \uparrow$ all spin up electrons
 $n=2$
 $l=1 \rightarrow m_l = -1, 0, 1$: each electron are in these three states.
 $\rightarrow m_l = (-1) + 0 + (+1) = \underline{0}$
 (total)

$\left(\begin{array}{ccc} 2 & 1 & 1/2 \\ 2 & 1 & 0 \\ 2 & 1 & -1/2 \end{array} \right)$
--

5. Compute the energy of the K_α X ray of sodium ($Z = 11$).

$$\text{Sodium } Z=11 \leadsto E(K_\alpha) = h \frac{m(Z-1)^2 e^4}{8 \epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{3cR(Z-1)^2}{4} = (10.2 \text{ eV})(Z-1)^2$$

$$\leadsto E(K_\alpha) = (10.2 \text{ keV}) 10^2 \quad \begin{matrix} 1 \leftarrow n_f \\ \leftarrow n_i \rightarrow 2 \end{matrix}$$

$$= \underline{\underline{1.02 \text{ keV}}} \quad (\text{Experiment: } 1.04 \text{ keV})$$

6. Some measured X-ray energies in silver ($Z = 47$) are $\Delta E(K_\alpha) = 21.990$ keV and $\Delta E(K_\beta) = 25.145$ keV. The binding energy of the K electron in silver is $E_b(K) = 25.514$ keV. From these data, find: (a) the energy of the L_α X ray, and (b) the binding energy of the L electron.

silver ($Z=47$)
 $\Delta E(K_\alpha) = 21.990$ keV
 $\Delta E(K_\beta) = 25.145$ keV
 $E_b(K) = 25.514$ keV
 binding energy
 \rightarrow energy: $-E_b(K) = E(K)$

see Fig 7.20

i) $E(L_\alpha) = ?$
 from figure
 $\Delta E(L_\alpha) + \Delta E(K_\alpha) = \Delta E(K_\beta)$
 $\rightarrow \Delta E(L_\alpha) = 25.145$ keV
 $- 21.990$ keV = 3.155 keV

ii) $\Delta E(K_\alpha) = E(L) - E(K)$
 $E(L) = \Delta E(K_\alpha) + E(K)$
 $= 21.990$ keV $- 25.514$ keV
 $= -3.524$ keV $\Rightarrow E_b(L) = -E(L) = \underline{\underline{3.544}}$ keV

Additional Materials