Hydrogenic and Multielectron Atoms and the Periodic Table

The Schrödinger equation governing the electrons in atoms is

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}=\frac{2M}{\hbar^2}\left[V(r)-E\right]\psi.$$

Where U(r) is the potential energy of the electron and E is the energy of the allowed levels.

Force, Orbits, Potential Energy and Total Energy

The single electron in hydrogen is in an electric potential created by the single proton. From electrostatics we know the Coulomb law:

$$F_{hydrogen}=\frac{kq_{p^+}q_{e^-}}{r^2}=-\frac{ke^2}{r^2}=-\frac{e^2}{4\pi\epsilon_0 r^2} \tag{1}$$

where the negative sign indicates that it is an attractive force between the electron and proton. For an atom with Z protons

$$F_Z=\frac{Zkq_{p^+}q_{e^-}}{r^2}=-\frac{Zke^2}{r^2}=-\frac{Ze^2}{4\pi\epsilon_0 r^2} \tag{2}$$

Applying Newton's Second Law (NSL) to the electron in a circular orbit about a proton gives (both inward, so they're negative)

$$F=m_e a_{cp}$$
$$-\frac{ke^2}{r^2}=-\frac{e^2}{4\pi\epsilon_0 r^2}=-m_e\frac{v^2}{r} \tag{3}$$

The potential energy is the negative of the work done by the (conservative) force (with the arbitrary constant of integration set to zero:

$$U_{hydrogen}(r)=-W_{hydrogen}=-\int\vec{F}_{hydrogen}\cdot d\vec{r}=-\int\frac{-ke^2}{r^2}\,dr=-\frac{ke^2}{r} \qquad \text{Potential Energy (4)}$$

The allowed energies, however, are harder to get at. In the square box with U = 0 within the box and U = ∞ outside, we required that the wave functions fit within the box. Here, we require that they fit around the circular orbit. That means we require the angular momentum of the electron be quantized. Thus, $p = m_e vr$ must be an integer multiple of ħ,

$$m_e vr=n\hbar \quad\Rightarrow\quad v=\frac{n\hbar}{m_e r} \tag{5}$$

Substituting this into NSL (3) gives a value for r

$$\frac{ke^2}{r^2}=\frac{m_e}{r}\left(\frac{n\hbar}{m_e r}\right)^2 \quad\Rightarrow\quad r=n^2\frac{\hbar^2}{ke^2 m_e} \tag{6}$$

When n = 1, this is the Bohr orbit, a_B:

$$a_B=\frac{\hbar^2}{ke^2 m_e}=\frac{\hbar^2}{4\pi\epsilon_0 e^2 m_e} \qquad \text{The First Bohr Orbit (7)}$$

The total energy of the electron in this orbit is

$$E = K + U = \frac{1}{2}m_e v^2 - \frac{ke^2}{r} \tag{8}$$

Substituting for $m_e v^2$ from NSL (3) gives

$$E = \frac{1}{2}\left(\frac{ke^2}{r}\right) - \frac{ke^2}{r} = -\frac{ke^2}{2r} \tag{9}$$

Substituting the value of r from (6) then gives

$$E_n = -\frac{1}{2}\frac{ke^2}{r} = -\frac{1}{2}ke^2\left(\frac{m_e ke^2}{n\hbar^2}\right) = -\frac{1}{2}\frac{m_e\left(ke^2\right)^2}{n^2\hbar^2} \tag{10}$$

Introducing the Rydberg Energy, (TZDII Eq. 5.22),

$$E_R = \frac{m_e\left(ke^2\right)^2}{2\hbar^2} = 13.6\text{eV} \tag{11}$$

we can write the energy of the n^{th} orbit as

$$E_n = -\frac{E_R}{n^2} \qquad \text{Allowed Energies (12)}$$

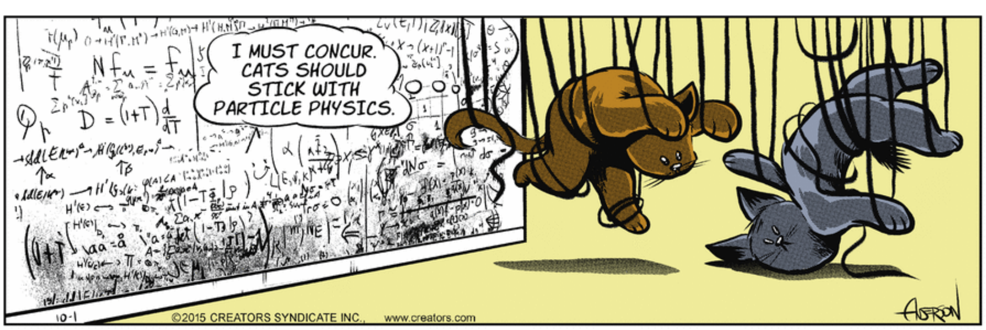
Hydrogenic Atoms

For atoms with Z > 1, replace ke^2 with Zke^2

$$U_Z\left(r\right) = -\frac{Zke^2}{r} \tag{13}$$

$$E_{n,Z} = -\frac{1}{2}\frac{m_e\left(Zke^2\right)^2}{n^2\hbar^2} = \frac{Z^2 E_R}{n^2} \tag{14}$$

$$a_{B,Z} = \frac{\hbar^2}{Zke^2 m_e} = \frac{a_B}{Z} \tag{15}$$



Multielectron Atoms

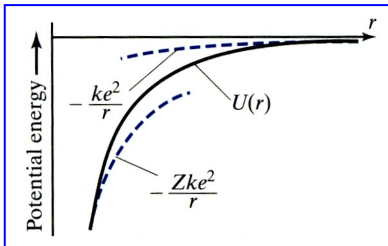


FIGURE 10.1
The IPA potential energy $U(r)$ of an atomic electron in the field of the nucleus plus the average distribution of the other $Z-1$ electrons. As $r \to \infty$, U approaches $-ke^2/r$; as $r \to 0$, U approaches $-Zke^2/r$ as in Eq. (10.5).

The independent particle approximation knits together the potentials of the innermost electron ($-Zke^2/r$) and the outermost ($-ke^2/r$) with

$$U_{Multielectron}(r) = -Z_{eff}\frac{ke^2}{r} \qquad (16)$$

For the orbital energies, replace ke^2 in the hydrogen equations with $Z_{eff}ke^2$:

$$E_{Multielectron}(r) = -Z_{eff}^2\frac{E_R}{n^2} \qquad (17)$$

For the outermost electron, $E_{Ionization} = -Z_{eff}^2 E_R / n^2$, allowing estimation of Z_{eff} from lab measurements of E_I.

This expression, with the variation in Z_{eff} due to the shielding of the nucleus by inner electrons, is what makes the energy levels slightly different for the s, p, d, and f levels as shown in Figure 10.3.

In hydrogen, the electrons in all the levels see the same nuclear charge but those with n > 1 are at lower energies because they are farther away from the nucleus. In multielecton (and multiproton) atoms, there is more nuclear charge for each additional electon, but most of that charge (not all of it … mostly $Z_{eff} > 1$) is shielded by inner electrons and they are farther away from the nucleus. For instance, the p electrons are fairly well shielded by the inner s electrons. But they are not very well shielded by the other p electrons.

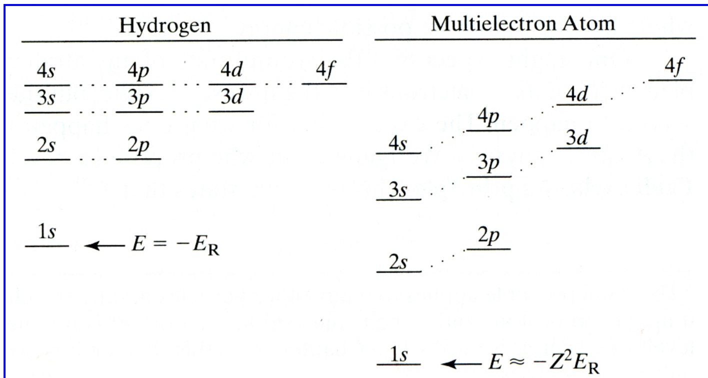
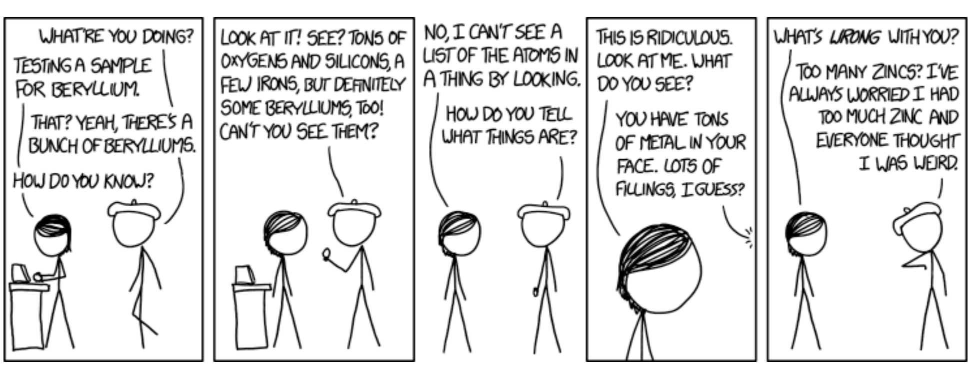


FIGURE 10.3
Schematic energy-level diagrams for a hydrogen atom and for one of the electrons in a multielectron atom. In hydrogen, all states with the same n are degenerate. In multielectron atoms states with lower l are more tightly bound because they penetrate closer to the nucleus. In many atoms this effect results in the $4s$ level being lower than the $3d$, as shown here.



The Quantum Periodic Table

n	**Alkali Metals**: Filled Shell + 1 Low Ionozation Energy, large radius	Closed S-Shell														**Halogens**: Filled Shell - 1 High electron affinity	Filled Shell: **Noble Gases**
n	s -shell		d and f shells filling										p-shell filling					
1	H																He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4/3	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5/4	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6/5/4	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7/6/5	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Some tables have all f-shell elee-ments in lower box

	f2	f3	f4	f5	f6	f7	f8	f9	f10	f11	f12	f13	f14	d1	
4	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	**Lanthanides: Rare Earths**
5	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	**Actinides**

Filled Shells have high ionization energy, low electron affinity, minimal radii

Noble Gases

Filled outer s- or p-shell, non-reactive

Halogens

Filled p-shell – 1

High electron affinity

Bind by borrowing e^-: e.g. NaCl

Alkalai Metals

Filled p-shell + 1

Low Ionization Energy

Largest atoms (outer e^- not tightly bound)

Bind by sharing outer e^-: e.g. H_2O, NaCl

Transition Elements

Those with an outer d-shell electron

Inner Transition Elements

Those with an outer f-shell electron

"Rats! I thought lanthanoids and actanoids were gonna be giant robots or something."