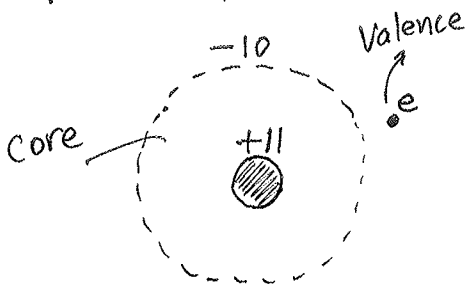


Let us introduce a few concepts regarding atomic shells and electron configurations; Atomic Core and Valence Electrons.

* Using Na ($Z=11$) as an example, the first 10 electrons fill in $1s^2 2s^2 2p^6$ shells, and the 11th electron in $3s$ or $3p$ or others.



The 10 electrons have strong interactions with the nucleus, and form a closed shell.

(The maximum number of electrons determined by Pauli Exclusion Principle is $2+8=10$ for the first two main shells $n=1, 2$)

Such a close shell (one nucleus with full shell electrons) is a stable structure, forming a core of the atom. We call this "Atomic Core".

* The electron outside the atomic core is called "valence electron". Atomic chemical properties and spectrum are mainly determined by this valence electron, since the interaction between the valence electron and this atomic core is not strong, the valence electron is easy to be excited to excited states or be ionized.

* Since the smallest orbits have been occupied by core electrons (electrons of the atomic core are called core electrons), the valence electron cannot occupy the smallest orbits any more. So it has to go to larger orbits (usually with larger quantum numbers of n and/or l).

Example: For Li atom, 2 electrons occupy $n=1$, then the 3rd one (valence electron) has to be on $n \geq 2$. This is why the Li energy levels start with $2s$, not $1s$.

Similarly, Na energy levels start with $n=3$, i.e., 3s
 K " " " " $n=4$, i.e., 4s
 Rb " " " " $n=5$, i.e., 5s
 Cs " " " " $n=6$, i.e., 6s

Only H and He can start with $n=1$ (1s or 1s²).

* Atomic spectrum is mainly determined by the valence electrons.
 So elements with same number of valence electrons have similar spectra and also similar chemical properties.

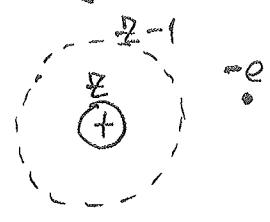
* Periodic Table of elements :

The arrangements of elements are mainly determined by the number of valence electrons, along with electron configurations. To determine the quantity of valence electrons, we should look at the vertical column of the periodic table.

Group	Quantity of valence electrons
Group 1 (I) (Alkali metals)	1
Group 2 (II) (Alkaline Earth metals)	2
Group 3-12 (Transition metals)	1 or 2
Group 13 (III) (Boron Group)	3
Group 14 (IV) (Carbo Group)	4
Group 15 (V) (Nitrogen Group)	5
Group 16 (VI) (Chalcogens)	6
Group 17 (VII) (Halogens)	7
Group 18 (VIII) (Noble Gases)	8* → Except for He, only 2 valence electrons

5. Shielding, Penetration, Atomic Core Polarization Effects.

(1) Shielding :

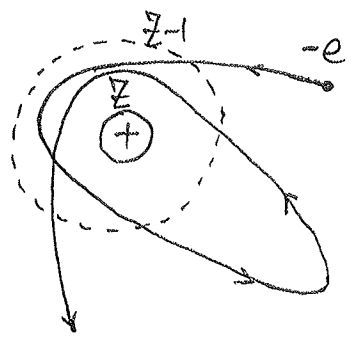


Let us consider the case of one valence electron (alkali atoms).

The inner electrons inside the atomic core will have shielding effect on the nucleus charge that the valence electron experienced.

Imagine this closed shell as a sphere with negative charges on the surface (e.g., 10 electrons of Na) and one positive charge at the center of the sphere (the nucleus with +11 charges). For the valence electron (the 11th) outside the sphere, the electron experiences a point charge at the center of the sphere with charge of +1, i.e., the atomic core charge $Z_a = 11 - 10 = +1$.

(2) Penetration :



However, the valence electron does not always stay outside the atomic core. As the calculation we made with QM in hydrogen atom, the valence electron does have probabilities to occur inside the atomic core.

This phenomenon is called penetration.

When penetration occur, inside the "sphere", the valence electron will experience larger nucleus charges, because the shielding effect is partially removed. Thus, the charge that a valence electron can experience

Z^* is determined by the average effect of the shielding when outside the atomic and the penetration inside the core: $1 \leq Z^* \leq Z$.

The actual Z^* depends on how much time the valence electron spends inside and outside the atomic core. Obviously, Z^* values depend on both n and l quantum numbers, as different n, l correspond to different electron orbitals that strongly affect the penetration possibilities. Z^* is called the effective charge.

Besides the effective charge Z^* , the penetration also affects the effective quantum number n^* for multielectron atoms. Recall the principal quantum number n in energy level

$$E_n = -Rhc \frac{Z^2}{n^2} \text{ is defined in hydrogen atom, i.e.,}$$

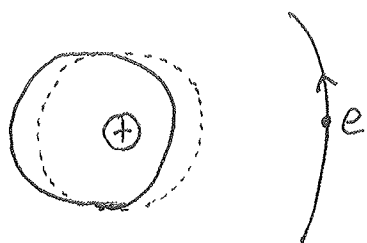
when electron has orbitals like hydrogen, it has full quantum number n . When penetration occurs, the valence electron's orbitals will be different from hydrogen electron orbitals. This causes the effective quantum number n^* to be smaller than n :

$$n^* = n - \delta_{nl},$$

where δ_{nl} is quantum defect and it varies with n and l for each element. Thus, for alkali atoms,

the energy levels $E_{nl} = -Rhc \frac{(Z^*)^2}{(n^*)^2}$, where Z^* and n^* are determined from experiments.

(3) Atomic Core Polarization effect:



Because of the Coulomb field produced by the valence electron, the charge distribution center of the atomic core will have displacement.

This causes the negative electrons' charge center ~~does~~ not overlap with the positive nucleus anymore. Thus, the atomic core is polarized and forms an electric dipole. This atomic core electric dipole interacts on the valence electron and results in extra Coulomb attraction. This causes the valence electron (also the atom) energy decreases, i.e., n^* becomes smaller, so the $E_{n\ell}$ becomes further negative.

Similarly, the reason that penetration causes n^* to be smaller than n is that the valence electron experiences extra Coulomb attraction, compared to full shielding, so resulting in lower energy \Rightarrow smaller n^* .

In summary,

$$\left. \begin{array}{l} \text{Shielding} \\ \text{Penetration} \end{array} \right\} \Rightarrow 1 \leq Z^* \leq Z \quad (\text{effective charge})$$

$$\left. \begin{array}{l} \text{Penetration} \\ \text{Atomic Core Polarization} \end{array} \right\} \Rightarrow 0 \leq n^* \leq n \quad (\text{effective quantum number})$$

6. Alkali Atomic Structure

Since alkali atoms have one valence electron, just like the hydrogen atom, they have very similar atomic structure as the hydrogen atom. This is also because the atomic core has a closed or filled shell, resulting in zero total orbital angular momentum and corresponding magnetic moment, zero spin angular momentum and corresponding magnetic moment. Thus, the major magnetic interaction in an alkali atom is determined by the valence electron's spin-orbit coupling: $\vec{S} + \vec{L} = \vec{J}$, forming fine structure. When considering nuclear spin, similar to hydrogen atom, alkali atoms will also have nuclear spin - electron total angular momentum coupling $\vec{I} + \vec{J} = \vec{F}$, and form hyperfine structure.

But there are also two major differences between the alkali atomic structure and the hydrogen:

- (1) Due to electrostatic interactions between electrons, though the mean electric field that the valence electron experiences is still a spherical symmetric field (central field) $V(r)$, it is not a Coulomb field $(-\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r})$, i.e., $V(r)$ does not have $-\frac{1}{r}$ format. Then as we pointed out earlier in the central field approximation, the energy levels depend on both n and l , i.e., different l s are now corresponding to different energy levels.

This is different from hydrogen atoms, where different l s under the same n are degenerate, i.e., they have the same energy eigenvalues. Thus, in the alkali atomic structure (e.g., Na), even before considering fine and hyperfine structures, the $3s$ and $3p$ levels are not degenerate.

(2) As just discussed above, shielding, penetration, and atomic core polarization effects cause alkali atoms to have effective charge Z^* and effective quantum number n^* . Both Z^* and n^* vary with elements and with n, l numbers. They need to be determined from measurements.

When using measured Z^* and n^* to replace Z and n , the energy levels that we derived for hydrogen atoms can be used to calculate alkali atomic energy levels.

* Fine structure of Alkali atoms:

Recall hydrogen fine structure

$$\Delta E_{ls} = \begin{cases} \frac{\alpha^4 Z^4 \mu c^2}{4n^3} \cdot \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, & l = 0 \end{cases}$$

Replace Z^4 with $Z_a^2 (Z^*)^2$ (where $Z_a = 1$), replace n^3 with $(n^*)^3$, and μ is the reduced mass for alkali atoms, then the alkali atoms fine structure

$$\Delta E_{ls} = \begin{cases} \frac{\alpha^4 Z_a^2 (Z^*)^2}{4(n^*)^3} \cdot \frac{j(j+1) - l(l+1) - s(s+1)}{l(l+\frac{1}{2})(l+1)}, & l \neq 0 \\ 0, & l = 0 \end{cases}$$

* Hyperfine Structure of Alkali Atoms:

① For $l=0$,

$$|\psi_s(0)|^2 = \frac{Z^* Z_a^2}{\pi a_1^3 (n^*)^3} \left(1 - \frac{d\delta}{dn}\right)$$

Where $n^* = n - \delta$ (δ is quantum defect).

$$\therefore \Delta E_M = \frac{1}{4\pi\epsilon_0 c^2} \left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right) \frac{8}{3} \frac{Z^* Z_a^2}{a_1^3 (n^*)^3} \left(1 - \frac{d\delta}{dn}\right) \\ * \frac{1}{2} [F(F+1) - j(j+1) - I(I+1)]$$

② For $l \neq 0$,

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^* Z_a^2}{a_1^3 (n^*)^3 (l + \frac{1}{2}) l(l+1)}$$

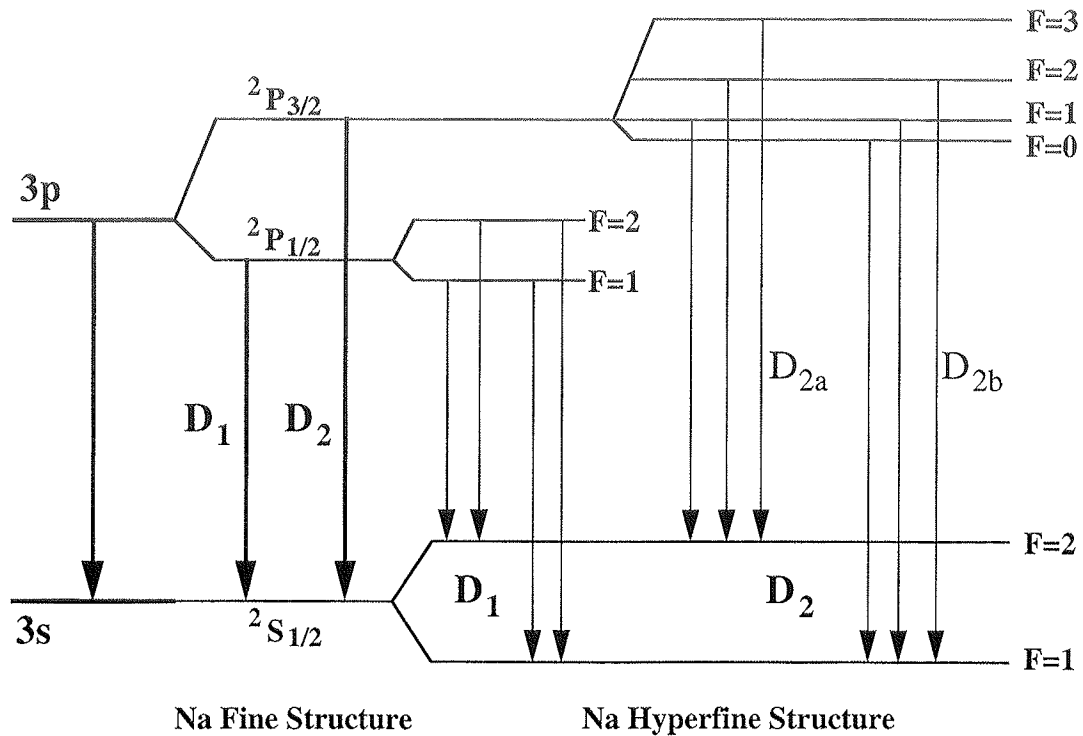
$$\therefore \Delta E_M = \frac{1}{4\pi\epsilon_0 c^2} \left(2\mu_B \frac{\mu_I}{\sqrt{I(I+1)}}\right) \left(\frac{Z^* Z_a^2}{a_1^3 (n^*)^3}\right) \frac{1}{(l + \frac{1}{2}) j(j+1)} \\ * \frac{1}{2} [F(F+1) - j(j+1) - I(I+1)]$$

* In magnetic field, alkali will also have Zeeman effect, similar to hydrogen situation.

Example, Quantum Defect of Na atom $\delta(n, l)$

$l \backslash n$	3	4	5	6	7	8
0	1.373	1.357	1.352	1.349	1.348	1.351
1	0.883	0.867	0.862	0.859	0.858	0.857
2	0.010	0.011	0.013	0.011	0.009	0.013
3	—	0.000	-0.001	-0.008	-0.012	-0.015

		$\delta_{fs}(cm^{-1})$	n^*	Z^*
Li	2P	0.34	1.966	2.060
Na	3P	17.20	2.116	3.531
K	4P	57.52	2.233	4.17
Rb	5P	237.60	2.286	5.83
Cs	6P	554.91	2.345	5.51



Energy Level Diagram of Atomic Na

Shown here is an example of Na atomic structure:

Ground State Electron Configuration: $1s^2 2s^2 2p^6 3s$

Ground State: $3s$

$$n=3, l=0, s=\frac{1}{2} \Rightarrow \hat{j} = l+s = \frac{1}{2} \Rightarrow 2S_{1/2}$$

$$\left. \begin{array}{l} \text{Na nuclear spin } I = \frac{3}{2} \\ \text{Total electron } \rightarrow \hat{j} = \frac{1}{2} \end{array} \right\} \Rightarrow \begin{array}{l} F = I + \hat{j} = 2 \\ F = I - \hat{j} = 1 \end{array}$$

First excited state: $3p$

$$n=3, l=1, s=\frac{1}{2} \Rightarrow \hat{j} = \begin{cases} l+s = \frac{3}{2} \Rightarrow 2P_{3/2} \\ l-s = \frac{1}{2} \Rightarrow 2P_{1/2} \end{cases}$$

$$\left. \begin{array}{l} I = \frac{3}{2} \\ \hat{j} = \frac{3}{2} \end{array} \right\} \Rightarrow F = 3, 2, 1, 0$$

$$\left. \begin{array}{l} I = \frac{3}{2} \\ \hat{j} = \frac{1}{2} \end{array} \right\} \Rightarrow F = 2, 1$$