Roadmap to the structure of *N*-electron atoms

Hydrogenic systems:

Quantum defect Foot 4.2

2-electron systems:

Perturbation treatment - very crude Foot 3.1

Antisymmetric wavefunctions - very important Foot 3.2.1

***N*-electron systems:**

Central field approximation Foot 4.3

Configurations Foot 4.1

The periodic table of elements

***LS*-coupling:** Foot 5

Detailed energy structure within a configuration

Electrostatic interaction in 2-electron systems.

Neglect finestructure just to simplify notations

$$(-\frac{\hbar^2}{2m}\hat{\nabla}_1^2-\frac{Ze^2}{4\pi\varepsilon_0\hat{r}_1}-\frac{\hbar^2}{2m}\hat{\nabla}_2^2-\frac{Ze^2}{4\pi\varepsilon_0\hat{r}_2}+\frac{e^2}{4\pi\varepsilon_0\hat{r}_{12}})\Psi(1,2)=E\cdot\Psi(1,2)$$

$$(\hat{H}_1+\hat{H}_2+\frac{e^2}{4\pi\varepsilon_0\hat{r}_{12}})\Psi(1,2)=E\cdot\Psi(1,2)$$

$$\hat{r}_{12}=|\hat{r}_1-\hat{r}_2|$$

First approximation: neglect the whole repulsion!!

$$\hat{H}_0=\hat{H}_1+\hat{H}_2$$

$$\hat{H}_i\phi_i(i)=E_i\phi_i(i),\ i=1,2.$$

$$E_i=-R\frac{Z^2}{n_i^2}$$

$$\phi_i(i)=R_{n_i\ell_i}(r_i)\cdot Y_{\ell_i,m_{\ell_i}}(\theta_i,\varphi_i)\cdot\chi_{m_{s_i}}(sz_i)$$

$$\Psi_0(1,2)=\phi_1(1)\cdot\phi_2(2)\quad (i)=(r_i,\theta_i,\varphi_i,sz_i)$$

$$E_0=E_1+E_2$$

First order perturbation calculation:

$$E=E_0+<\frac{e^2}{4\pi\varepsilon_0 r_{12}}>_{\Psi_0}$$

Table 2.2 Radial hydrogenic wavefunctions $R_{n,l}$ in terms of the variable $\rho = Zr/(na_0)$, which gives a scaling that varies with n. The Bohr radius a_0 is defined in eqn 1.40.

$$R_{1,0} = \left(\frac{Z}{a_0}\right)^{3/2} 2\,\mathrm{e}^{-\rho}$$

$$R_{2,0} = \left(\frac{Z}{2a_0}\right)^{3/2} 2\,(1-\rho)\,\mathrm{e}^{-\rho}$$

$$R_{2,1} = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{2}{\sqrt{3}}\,\rho\,\mathrm{e}^{-\rho}$$

$$R_{3,0} = \left(\frac{Z}{3a_0}\right)^{3/2} 2\left(1-2\rho+\frac{2}{3}\rho^2\right)\mathrm{e}^{-\rho}$$

$$R_{3,1} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3}\,\rho\left(1-\frac{1}{2}\rho\right)\mathrm{e}^{-\rho}$$

$$R_{3,2} = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{3\sqrt{5}}\,\rho^2\,\mathrm{e}^{-\rho}$$

Normalisation: $\displaystyle\int_0^\infty R_{n,l}^2\, r^2\,\mathrm{d}r = 1$

Antisymmetric wavefunctions

A particle with half integer spin (fermion) must be described by an antisymmetric wavefunction

$$\Psi(\bar{q}_1,\bar{q}_2)=\frac{1}{\sqrt{2}}[\phi_1(1)\cdot\phi_2(2)-\phi_1(2)\cdot\phi_2(1)]$$

coordinates

quantum numbers

$$\bar{q}=(r,\theta,\varphi,sz)$$

$$\phi_i=R_{n_i\ell_i}(r_j)\cdot Y_{\ell_i,m_{\ell_i}}(\theta_j,\varphi_j)\cdot\chi_{m_{s_i}}(sz_j)$$

$$i=1,2. \quad j=1,2.$$

- $1/\sqrt{2}$ due to normalisation
- $\Psi(\bar{q}_2,\bar{q}_1)=-\Psi(\bar{q}_1,\bar{q}_2)$
- "+" sign will give the symmetric function
- 2 electrons cannot have ALL 4 quantum numbers equal => Pauli principle

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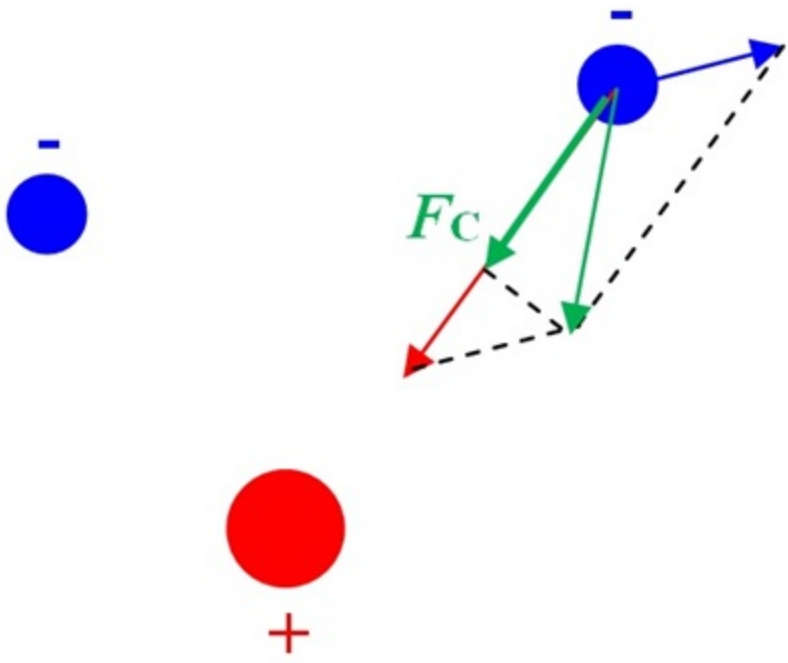
Detailed energy structure within a configuration

The central field approximation
N-electron atoms

- **Each electron moves independently of the others in the electrostatic field from the nucleus and the other N - 1 electrons.**

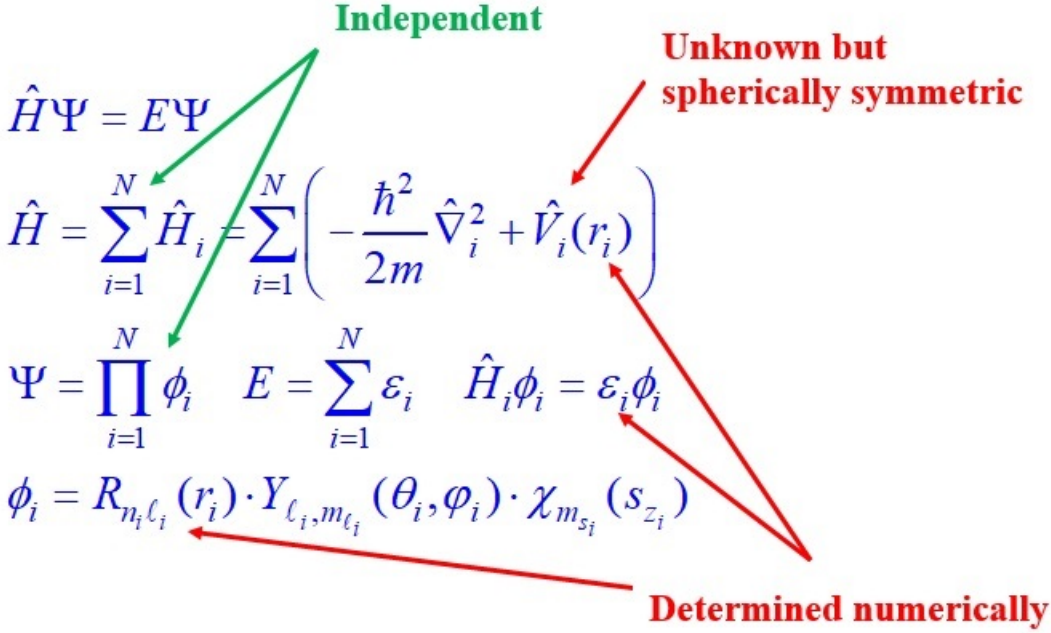
- **This field is assumed to be spherically symmetric.**



The central field approximation

- **Each electron moves <u>independently</u> of the other in the electrostatic field from the nucleus and the other N - 1 electrons.**

- **This field is assumed to be <u>spherically symmetric.</u>**



(Physically acceptable wavefunctions Ψ must then be anti-symmetrized.)

One-electron atoms in spherical coordinates

$$H = -\frac{\hbar^2}{2\mu}\cdot\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{Ze^2}{4\pi\varepsilon_0\cdot r}$$

$$= -\frac{\hbar^2}{2\mu}\cdot\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2}+\frac{1}{\tan\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right)\right]-\frac{Ze^2}{4\pi\varepsilon_0\cdot r}$$

$$= -\frac{\hbar^2}{2\mu}\cdot\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{L^2}{2\mu\cdot r^2}-\frac{Ze^2}{4\pi\varepsilon_0\cdot r}$$

Generally, any spherical potential, $U(\vec{r})=U(r)$

$$\Psi(r,\theta,\varphi,sz)=R_{n,\ell}(r)\cdot Y_{\ell,m_l}(\theta,\varphi)\cdot\chi_{s,m_s}(sz)$$

Self consistent field technique.

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i = \sum_{i=1}^{N} \left(-\frac{\mathrm{h}^2}{2m} \hat{\nabla}_i^2 + \hat{V}_i(r_i) \right)$$

$$E = \sum_{i=1}^{N} \varepsilon_i \quad \hat{H}_i \phi_i = \varepsilon_i \phi_i$$

$$\phi_i = R_{n_i l_i}(r_i) \cdot Y_{l_i, m_{l_i}}(\theta_i, \varphi_i)$$

1. Guess $R_{\mathrm{i}}(r_{\mathrm{i}})\ i = 1, 2, \ldots N$
2. Calculate the potential, V_{i}, experienced by electron i due to the attraction of the nucleus and the repulsion from the charge distributions, $e \cdot \left|\phi_{\mathrm{j}}\right|^2 \ j \neq i$, of the other N-1 electrons. (see Ex 25, H2)
3. Solve $\hat{H}_{\mathrm{i}} \phi_{\mathrm{i}} = \varepsilon_{\mathrm{i}} \phi_{\mathrm{i}}$ numerically $\Rightarrow R_{\mathrm{i}}$ and ε_{i}
4. Repeat 3 for all N electrons $\Rightarrow$ improved $R(r)$.
5. Iterate from 2 until energies and wavefunctions reach a desired consistency.

Ionization energies (cm^{-1}) in He-like systems in different approximations.

$$E_{\text{ion}}^{\text{He}} = \left| E_{\text{He}}(1s^2) - E_{\text{He}^+}(1s) \right| = \left| E_{\text{He}}(1s^2) - R\frac{Z^2}{1^2} \right|$$

Approx	He I	ΔE / %	C V	ΔE / %
E_0	438920	-	3950352	-
E_1	164605	17	3127370	1.1
E_{CFA}	189116	4.6	3163975	0.05
E_{exp}	198310.66637(20)[a]		3162408(20)[b]	

E_0: No repulsion at all! $E(1s^2) = -2 \cdot R \cdot \frac{Z^2}{1^2}$

E_1: First order perturbation. $E(1s^2) = -2 \cdot R \cdot \frac{Z^2}{1^2} + \frac{5}{4} R \cdot Z$

E_{CFA} Central field approximation

[a] D. Z. Kandula *et al.*, Phys. Rev. Lett. **105**, 063001 (2010)

[b] L. Engström *et al.*, J. Phys. B: At. Mol. Opt. Phys. **25**, 2459 (1992)

Note that since binding energies scale with Z^2 and the electron repulsion only as Z, the CFA gets better as Z increases along an isoelectronic sequence

The CFA leads naturally to the concept of a configuration, i.e. a list of the n and ℓ quantum numbers for all electrons:

$$(n_1\ell_1)^{w_1}(n_2\ell_2)^{w_2}\cdot\ldots\ldots\cdot(n_m\ell_m)^{w_m}$$

where w is the number of equivalent electrons (having the same n and ℓ) in the orbital.

Compare with $\Psi = \prod_{i=1}^{N} \phi_i$

The configuration has a single energy value $E = \sum_{i=1}^{N} \varepsilon_i$ **beeing sum of the energies of all electrons involved.**

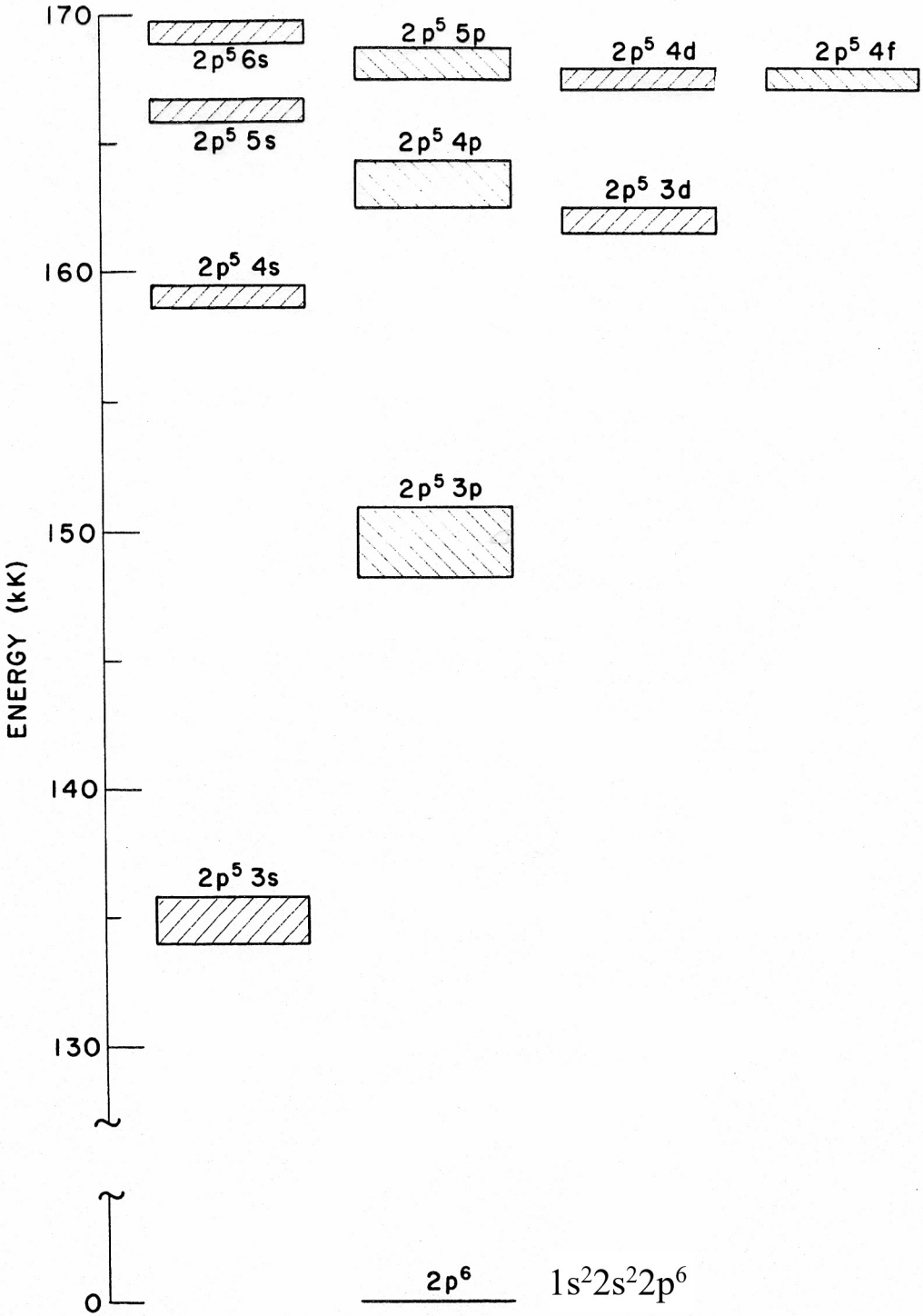
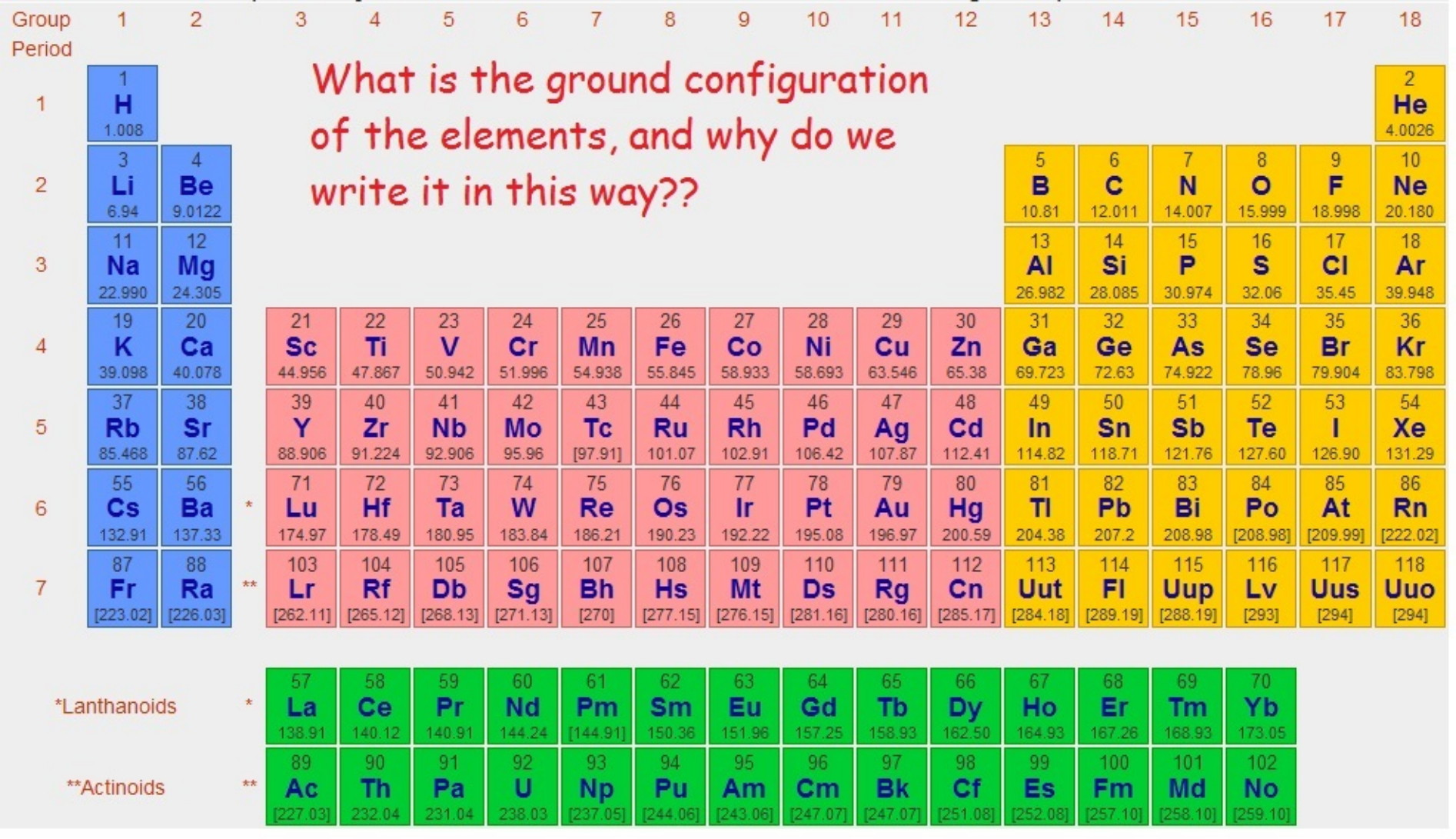


Fig. 4-1. Block diagram of the lowest configurations of Ne I. The levels of each configuration lie within the limited energy range shown by the corresponding shaded block. (There is one level in $2p^6$, and there are four levels in each p^5s configuration, ten levels in each p^5p, and twelve levels in each p^5d or p^5f configuration.)


What is the ground configuration of the elements, and why do we write it in this way??

The physical background to the periodic table of the elements.

1. Number of quantum states N:

   a) Given n and ℓ. Orbital / subshell

   $N = 2 \cdot (2\ell + 1)$ due to m_s and m_ℓ.

   b) Given n. Shell

   $N = 2n^2$

$$N = \sum_{\ell=0}^{n-1} 2(2\ell+1) = \sum_{\ell=0}^{n-1} 4\ell + \sum_{\ell=0}^{n-1} 2 = 4\frac{n(n-1)}{2} + 2n = 2n^2$$

2. Highest binding energy for low n and ℓ due to the quantum defect

3. Pauli principle, i.e. antisymmetric wave-functions, demanding that no 2 electrons have all 4 quantum numbers identical

Periodic System (first four rows)

H 1s																He $1s^2$	Filled K-shell
Li 2s	Be $2s^2$										B 2p	C $2p^2$	N $2p^3$	O $2p^4$	F $2p^5$	Ne $2p^6$	Filled L-shell
Na 3s	Mg $3s^2$										Al 3p	Si $3p^2$	P $3p^3$	S $3p^4$	Cl $3p^5$	Ar $3p^6$	8 outer electrons $3s^2 3p^6$
K 4s	Ca $4s^2$	Sc 3d	Ti $3d^2$	V $3d^3$	Cr $3d^4$	Mn $3d^5$	Fe $3d^6$	Co $3d^7$	Ni $3d^8$	Cu $3d^9$	Zn $3d^{10}$	Ga 4p	Ge $4p^2$	As $4p^3$	Se $4p^4$	Br $4p^5$	Xe $4p^6$	8 outer electrons $4s^2 4p^6$

.....

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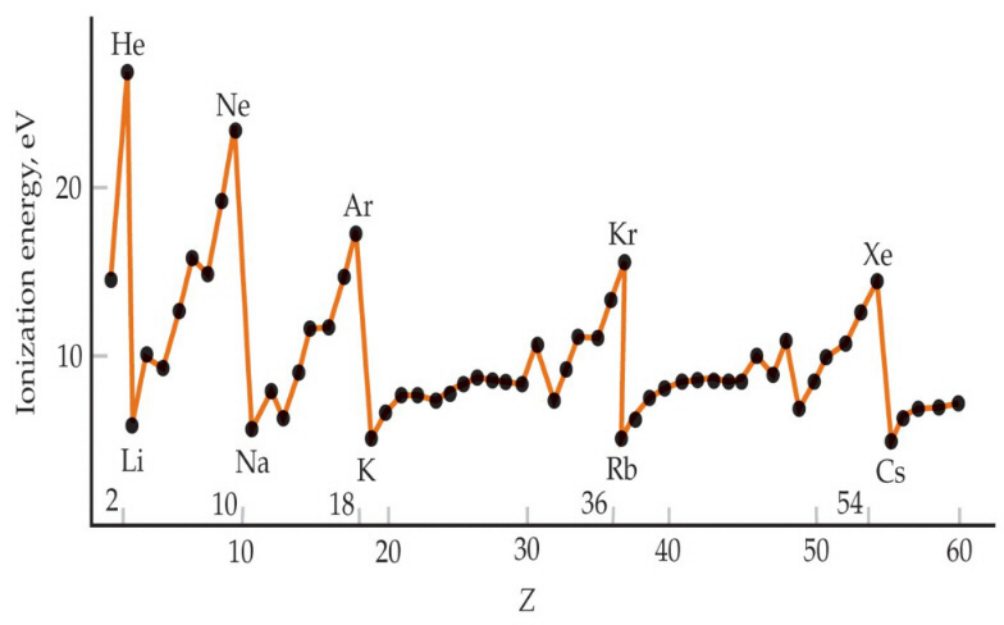
Alkali metals

Alkaline earths

Halogens

Noble gases


He
Ne
Ar
Kr
Xe
Li
Na
K
Rb
Cs
Ionization energy, eV
20
10
2
10
18
36
54
10
20
30
40
50
60
Z