

The shell model and alkali spectra

- So far we discussed hydrogen like atoms. This is a two particles problem.
- Can be solved exactly through the center of mass.
- Other atoms are many body systems. The solution can be found only by approximations.

The central field approximation:

- An atom with N electrons with nuclear charge +Ze. N=Z – neutral atom.
- An additional term of the Hamiltonian:

$$\hat{H} = \sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i>j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

- The subscripts i,j refers to individual electrons.

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$$

The eqn. can not be solved exactly.

- Main problem: The interaction related to two electrons. The separation to single variable eqns. Is not possible.
- Second problem: e-e interaction same order of magnitude as the e-n interaction:
- Perturbation theory – not suitable.

The Hartree approximation:

- A self consistent approach: We shall use a shortened terminology:
- The core of the Hartree approximation is:
- The inter-electron repulsion – contains a large spherically symmetric component.
- The self consistent potential energy is spherical symmetric.
- The I^{th} electron moves in the field of the nucleus and the other $N-1$ electrons
- We start with the wave functions of the N^{th} hydrogenic atom,

Using shortened terminology

- The approximated Hamiltonian is written as:

$$H = H^* + H_1$$

- Where:

$$H^* = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i)$$

- And:

$$\sum_i U(r_i) = -\sum_{i=1}^N \frac{Ze^2}{r_i} + \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle$$

Non spherical symmetric perturbation:

$$H_1 = \sum_{i<j}^N \frac{e^2}{r_{ij}} - \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle$$

U is a single electron operator:

- The many body Schrodinger eqn. is:

$$H^* \Phi = \left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i) \right\} \Phi = E \Phi$$

Φ is a product of single electron wave function ϕ_i .

- Coordinates of electrons are independent variables – A set of N independent eqns.

$$H_1^* \phi_1 = E_1 \phi_1 \quad ; \quad H_2^* \phi_2 = E_2 \phi_2 \quad ; \quad \dots$$

- When

$$H^* = \sum_{i=1}^N H_i^* \quad ; \quad E = \sum_i E_i$$

The Hartree method is a self consistent field method:

- Start with N-1 single electron wave functions. Their field on the Nth electron is

- Calculated $\left\langle \sum_{i < j}^N \frac{e^2}{r_{ij}} \right\rangle$

- The Schrodinger eqn for the Nth electron is solved to get an improved wave-function of the Nth electron.
- The procedure is repeated for the other N-1 electrons

This is an iterative technique.

- The first improved wave functions are used again to calculate the improved central field and so on.
- The procedure stops when the central field is consistent with the approximated wave function.
- The Hartree approximation resulted in many density functional theories and has a tremendous impact.

We end with many single electrons Schrödinger eqn.

- For each i -th electron:

$$\psi_i(\mathbf{r}_i) \equiv \psi(r_i, \theta_i, \phi_i) = R_i(r_i) Y_i(\theta_i, \phi_i).$$

Similar to the hydrogen atom:

$$\hat{L}_i^2 Y_{l_i, m_i}(\theta_i, \phi_i) = \hbar^2 l_i(l_i + 1) Y_{l_i, m_i}(\theta_i, \phi_i)$$

$$\left(-\frac{\hbar^2}{2m} \frac{1}{r_i^2} \frac{d}{dr_i} \left(r_i^2 \frac{d}{dr_i} \right) + \frac{\hbar^2 l_i(l_i + 1)}{2mr_i^2} + V_{\text{central}}(r_i) \right) R_i(r_i) = E_i R_i(r_i)$$

solutions are characterized by 4 quantum numbers:

- l and m_l , they are quantum numbers for each electron.
- n comes from the solution of the radial equation with the central field potential.
- m_s is the spin quantum number.
- The energy (and the other characteristics) of the many body atom is found by summarizing the values for all the electrons.

The reason for the success of the central field approximation:

- The electrons in the atom are ordered in shells.
- Almost all the electrons are inside closed, spherical sub-shells, and all the non radial interactions are averaged out.
- The off radial interactions from the unfilled shells are relatively small.

The shell model and the periodic table.

- The atomic states characterized by the quantum numbers:

Quantum number	symbol	Value
principal	n	any integer > 0
orbital	l	integer up to $(n - 1)$
magnetic	m_l	integer from $-l$ to $+l$
spin	m_s	$\pm 1/2$

Table 4.1: Quantum numbers for electrons in atoms.

Spectroscopic notation:

- $l = 0, 1, 2, 3, \dots$ are called *s, p, d, f, \dots* electrons

Gross and fine structure

- In hydrogenic atom the gross structure depends only on n . In other atoms – also on l .
- Without fine structure and external magnetic fields, each n, l level is degenerate.
- Each n, l term in the gross structure has $2(2l+1)$ degenerate levels.
- In the shell model we take into account only the gross structure.
- **Recall:** $Z^2 \alpha^2 = (Z^2/137)^2 \sim 10^{-4} Z^2$.
- **Fine structure is small. More significant at large Z**

The electrons are filled one by one

- It started as an empirical fact starting from the periodic table of elements:
- Stable configuration – with 2, 8 and 18 electrons.
- The Zeeman effect on Alkali metal atoms with a certain n - # of levels equal to the number of electrons in the closed shell of the noble gas of the same n .
- This led to the Pauli exclusion principle: We can only put a single electron in any quantum state. The spin is also a quantum #

The consequence of the Exclusion principle:

- In multi-electron system the electrons are indistinguishable.
- The probability distribution should be independent of permutation.

$$P(\dots, x_a, \dots, x_b, \dots) = |\Psi(\dots, x_a, \dots, x_b, \dots)|^2$$

$$P(\dots, x_a, \dots, x_b, \dots) = P(\dots, x_b, \dots, x_a, \dots)$$

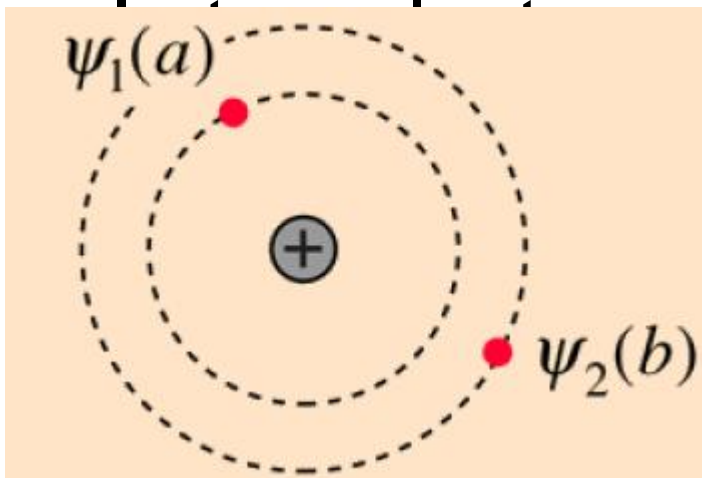
- This is possible only if:

$$\Psi(\dots, x_b, \dots, x_a, \dots) = e^{i\phi} \Psi(\dots, x_a, \dots, x_b, \dots)$$

- For Fermions (electrons) $\Phi = \pi$.

The wavefunction is asymmetric.

- It is consistent with the Pauli principle:



the wavefunction:

$$\psi = \psi_1(a)\psi_2(b)$$

Antisymmetric combination

$$\psi = \psi_1(a)\psi_2(b) \pm \psi_1(b)\psi_2(a)$$

- Is zero if a and b are equal.

The atomic shells:

- we can order the energies according to the quantum numbers n and l .
- As we add electrons, they fill up the lowest available shell until it is full.

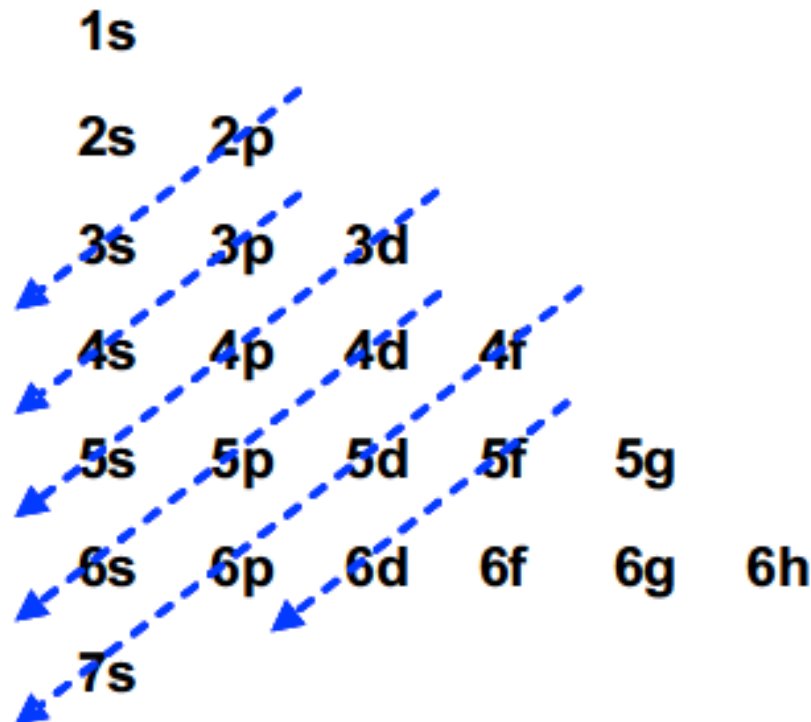
Shell	n	l	m_l	m_s	N_{shell}	N_{accum}
1s	1	0	0	$\pm 1/2$	2	2
2s	2	0	0	$\pm 1/2$	2	4
2p	2	1	-1, 0, +1	$\pm 1/2$	6	10
3s	3	0	0	$\pm 1/2$	2	12
3p	3	1	-1, 0, +1	$\pm 1/2$	6	18
4s	4	0	0	$\pm 1/2$	2	20
3d	3	2	-2, -1, 0, +1, +2	$\pm 1/2$	10	30
4p	4	1	-1, 0, +1	$\pm 1/2$	6	36
5s	5	0	0	$\pm 1/2$	2	38
4d	4	2	-2, -1, 0, +1, +2	$\pm 1/2$	10	48
5p	5	1	-1, 0, +1	$\pm 1/2$	6	54
6s	6	0	0	$\pm 1/2$	2	56
4f	4	3	-3, -2, -1, 0, +1, +2, +3	$\pm 1/2$	14	70
5d	5	2	-2, -1, 0, +1, +2	$\pm 1/2$	10	80
6p	6	1	-1, 0, +1	$\pm 1/2$	6	86
7s	7	0	0	$\pm 1/2$	2	88

Building the periodic table:

- Unfilled shell – normally with the lowest n but not always.
- Exceptions: The 19th electron goes into 4s shell rather than 3d shell.
- The 37th electron goes into 5s shell rather than 4d shell.
- The energy of a shell with large l value might be larger than a shell with larger n value but smaller l .

The process of filling the shells

- The nl sub-shells are filled diagonally when laid out in rows determined by the principal quantum number



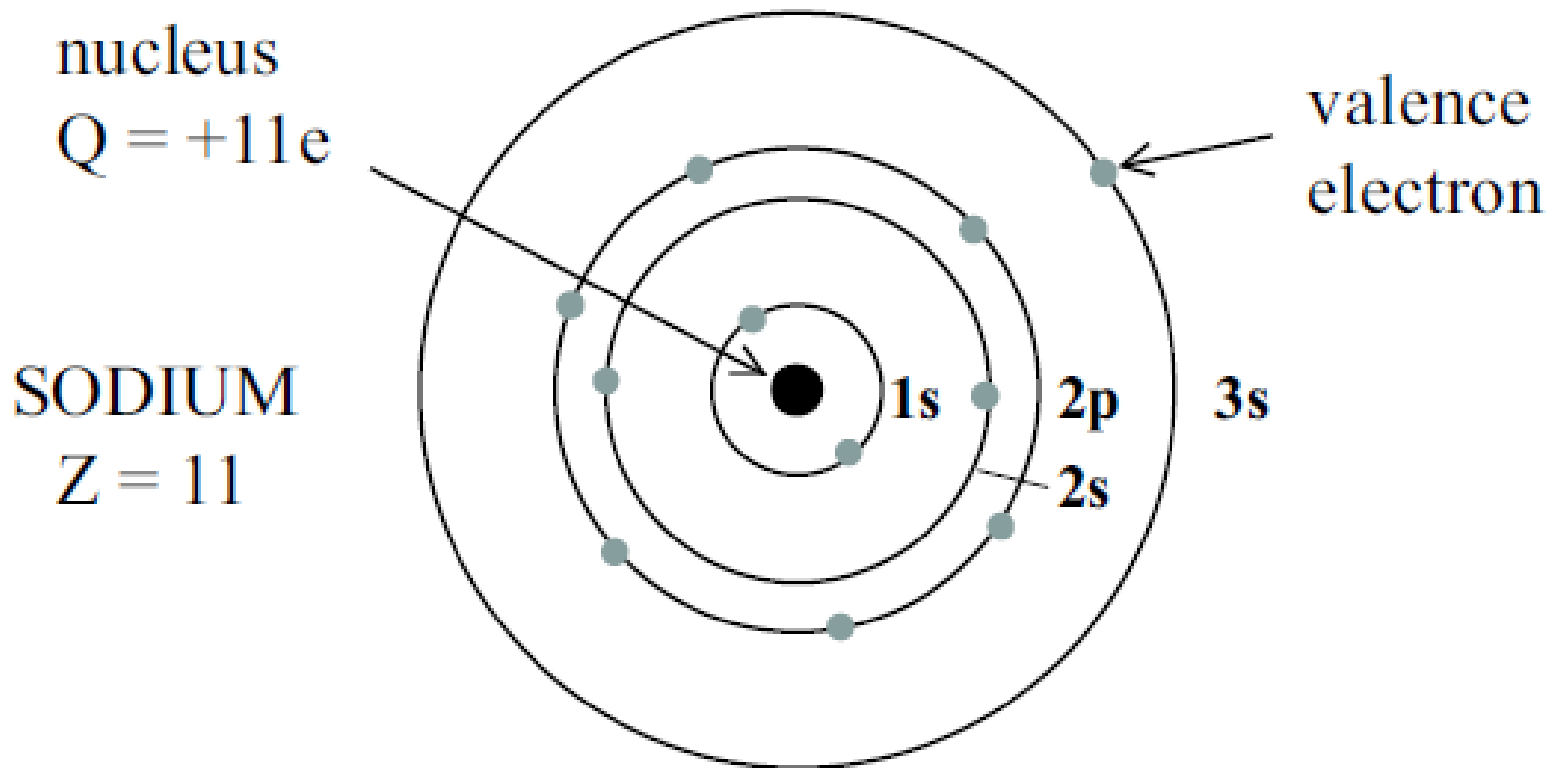
The electronic structure of the elements:

- First 11 elements:

Element	Atomic number	Electronic configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s^2 2s^1$
Be	4	$1s^2 2s^2$
B	5	$1s^2 2s^2 2p^1$
C	6	$1s^2 2s^2 2p^2$
N	7	$1s^2 2s^2 2p^3$
O	8	$1s^2 2s^2 2p^4$
F	9	$1s^2 2s^2 2p^5$
Ne	10	$1s^2 2s^2 2p^6$
Na	11	$1s^2 2s^2 2p^6 3s^1$

Screening of nuclear charges

- The inner shells screen the nuclear charge.
- For example the electronic configuration of Na.



Calculation of energy levels and radii.

- Sodium: atomic # of 11.
- Nuclear charge $+11e$, 11 electrons with total charge $-11e$.
- Recall, according to Bohr's model:

$$r_n = \frac{n^2}{Z} a_H,$$
$$E_n = - \left(\frac{Z}{n} \right)^2 R_H,$$

$$a_H = 5.29 \times 10^{-11} \text{ m}$$

$R_H = 13.6 \text{ eV}$ is the Rydberg constant.

Each electron shell screens completely a nuclear charge of the charge of the shell.

- $n=1$ shell – first 2 electrons. They see $+11e$ charge. $n=1$, $Z=11$ gives:
- $R_1 = 1^2 / 11 \times a_H = 0.05 \text{ \AA}$.
- $E_1 = -11^2 R_H = -1650 \text{ eV}$
- $n=2$ shell – next 8 electrons. Assuming shielding of the $n=1$ shell we have:

$Z_{\text{eff}} = +9$: Thus, $r_2 = 2^2 / 9 \times a_H = 0.24 \text{ \AA}$ and

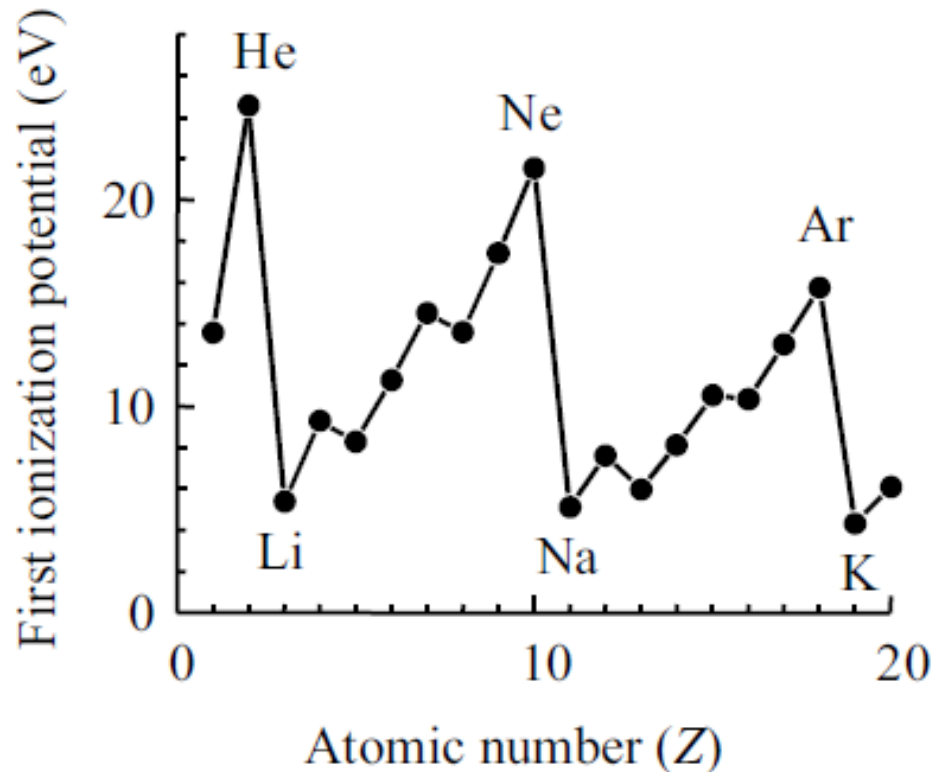
$$E_2 = -(9/2)^2 R_H = -275 \text{ eV}.$$

One outermost electron is left:

- $n=3$. The shells $n=1, 2$ are closed. Thus,
- $Z_{eff}=1$. Thus, $r_3=4.8 \text{ \AA}$ and $E_3=-1.5 \text{ eV}$.
- The treatment is crude, because it is based on the Bohr model, but it can be improved.

Experimental evidence for the shell model

- Ionization potentials and atomic radii
- Noble gas elements – highest ionization potential.

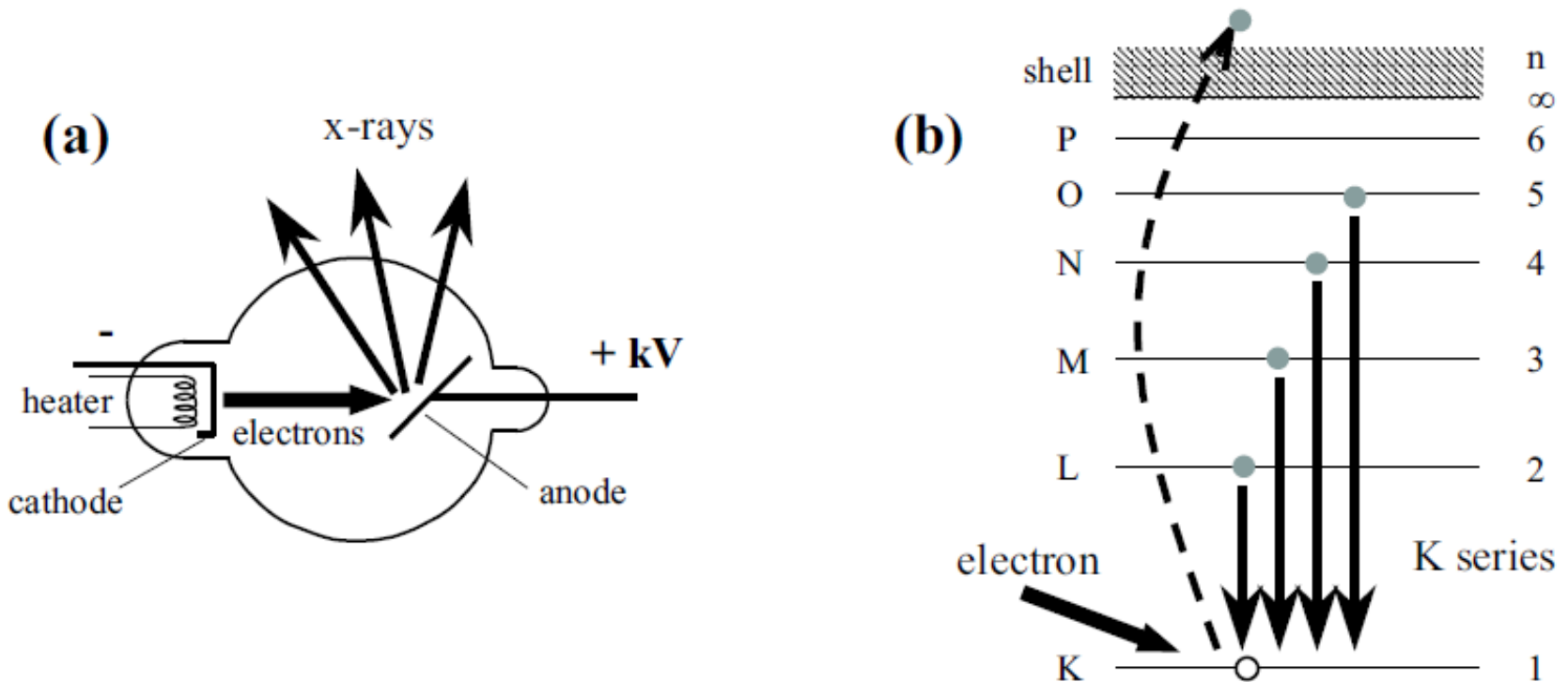


He, Ne and Ar has a closed shell

- High stability –large ionization potential.
- Removing an electron from alkali metals (Li, Na, K) gives a close shell ion – low ionization potential.
- Additional evidence, atomic radius measured by x-ray crystallography. Alkali metals – large radius – in accordance with low ionization potential.

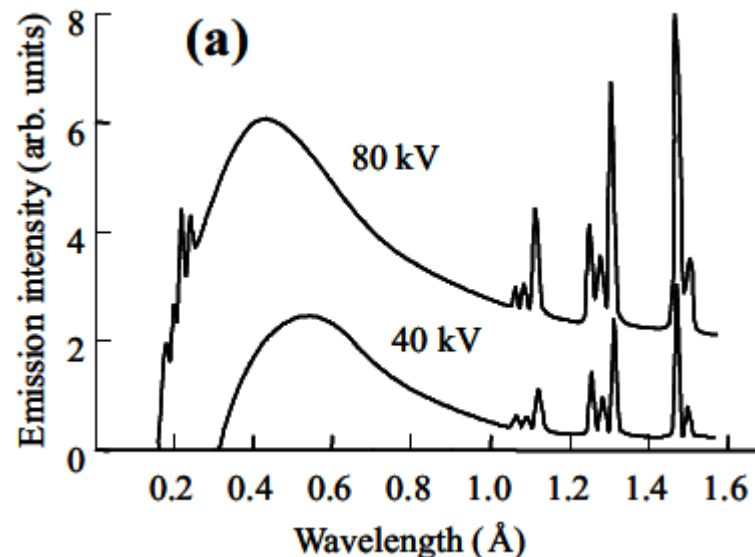
X-ray line spectra

- Enables a direction measurement of the energies of the inner shells.
- Experimental arrangement and measurement process:



The discrete emission lines are on top of a continuous emission

- The bremsstrahlung occurs when the electron is decelerated by interaction – without emission of core electrons.
- Ofcourse conservation of energy requires that $h\nu \leq eV$ (V is the voltage on the tube).



As the voltage increases inner shells are excited.

- The energy of the electron in the inner shell is:

$$E_n = -\frac{Z_n^{\text{eff}^2}}{n^2} R_H$$

- Z_n^{eff} is the effective nuclear charge after screening.
- The energy of the optical transition:

$$h\nu = |E_{n'} - E_n| = \left| \frac{Z_n^{\text{eff}^2}}{n^2} - \frac{Z_{n'}^{\text{eff}^2}}{n'^2} \right| R_H$$

Moseley law:

- Henry Moseley Found the empirical law which was a great support for Bohr's theory.
- We make the approximation: $Z_n^{\text{eff}} = Z_{n'}^{\text{eff}}$ and write both as $(Z - \sigma_n)$
- We get for K shell lines:

$$\frac{hc}{\lambda} \approx (Z - \sigma_K)^2 R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right)$$

where $n > 1$ and $\sigma_K \sim 3$.

- The reason why it works is that the dominant contribution of the lower level is taking over

The phenomenological screening parameter σ

- The L shell spectra obey:

$$\frac{hc}{\lambda} \approx (Z - \sigma_L)^2 R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

- For $n > 2$, and $\sigma_L \sim 10$.

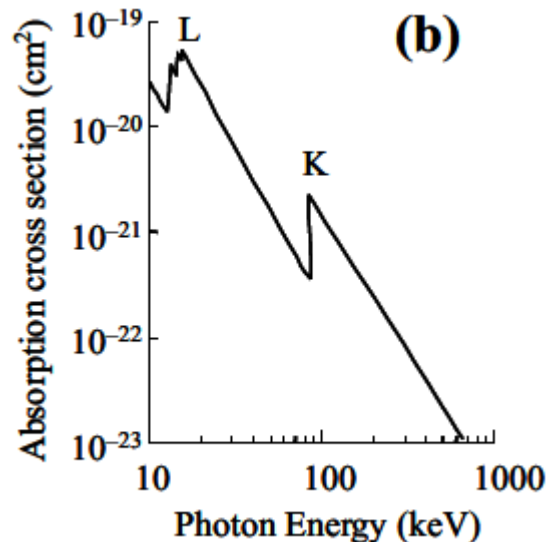
- The results are in agreement with the Bohr model, just with $Z - \sigma$ instead of Z .

X ray absorption:

final state, either - excited states of the valence electrons or - continuum above the ionization limit.

- Negligible binding energy, thus we put $E_n' = 0$

$$h\nu^{\text{edge}} = \frac{Z_{\text{eff}}^2}{n^2} R_H \equiv \frac{(Z - \sigma_n)^2}{n^2} R_H$$



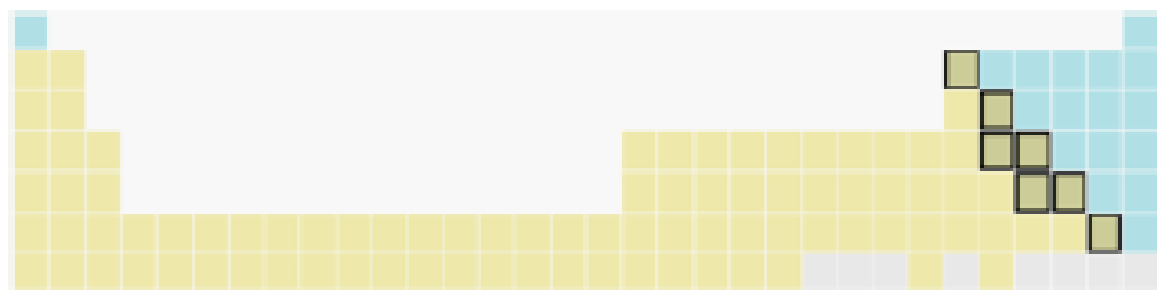
- In lead:

Strongest and most important experimental proof – the periodic table

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period ↓ 1	1 H																		2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F		10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl		18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br		36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I		54 Xe
6	55 Cs	56 Ba	57 La *	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At		86 Rn
7	87 Fr	88 Ra	89 Ac *	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts		118 Og
				* 58 Ce	* 59 Pr	* 60 Nd	* 61 Pm	* 62 Sm	* 63 Eu	* 64 Gd	* 65 Tb	* 66 Dy	* 67 Ho	* 68 Er	* 69 Tm	* 70 Yb	* 71 Lu		
				* 90 Th	* 91 Pa	* 92 U	* 93 Np	* 94 Pu	* 95 Am	* 96 Cm	* 97 Bk	* 98 Cf	* 99 Es	* 100 Fm	* 101 Md	* 102 No	* 103 Lr		

Mendelyev-periodic changes in chemical behavior.

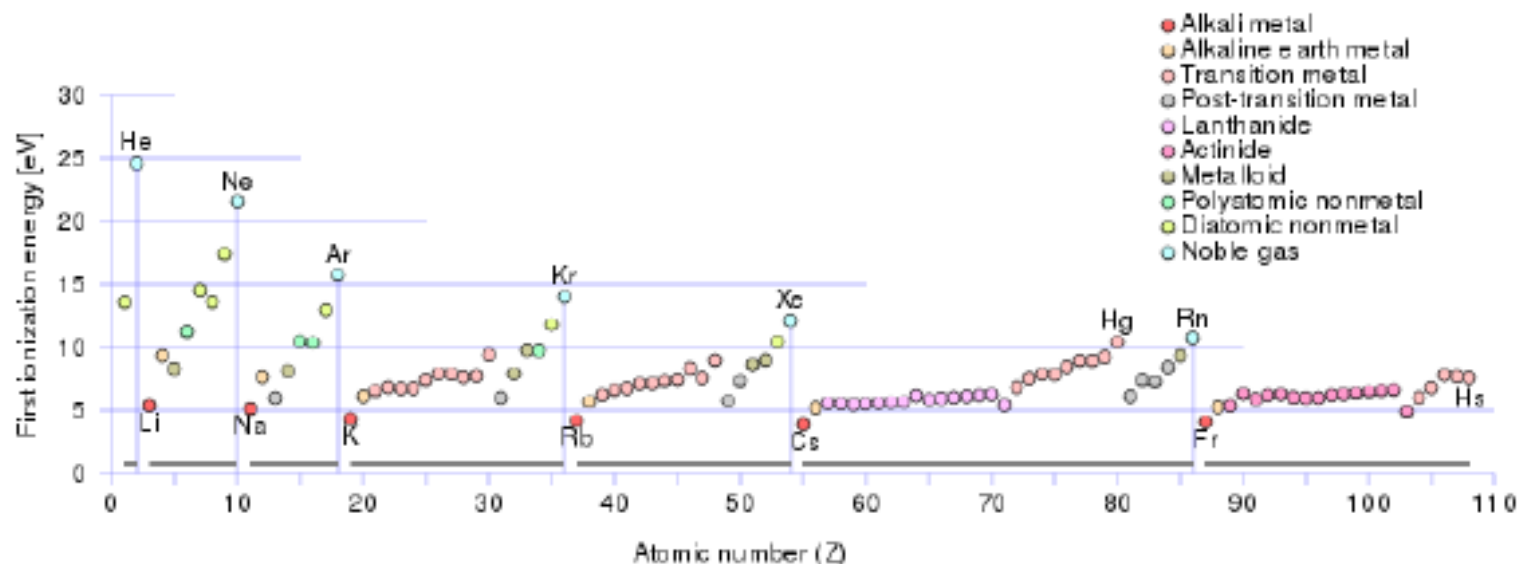
- Element at the same column are chemically similar.
- #18 – noble gases – chemically inert.
- Column #1 Alkali metals, ionic bonds, salts,
- Most elements are metals



Metals, metalloids, nonmetals, and elements with unknown chemical properties in the periodic table. Sources disagree on the classification of some of these elements.

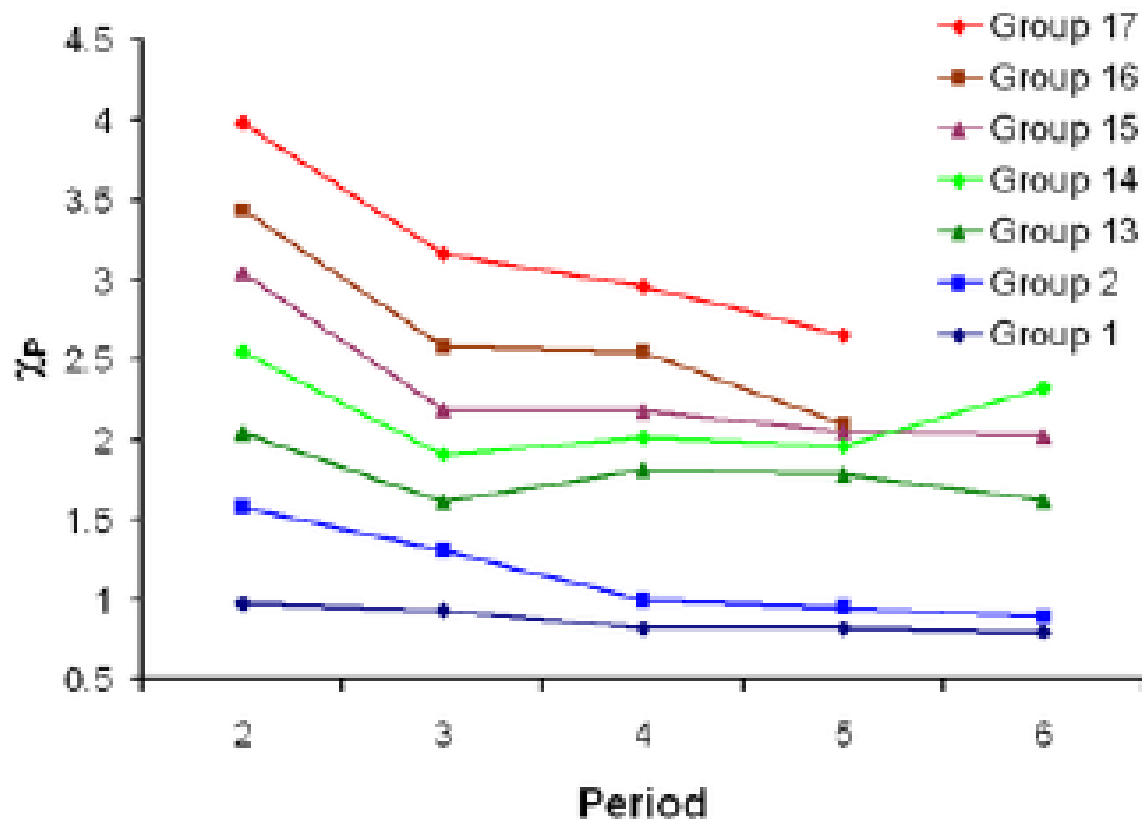
Periodic chemical behavior:

- Ionization energy:



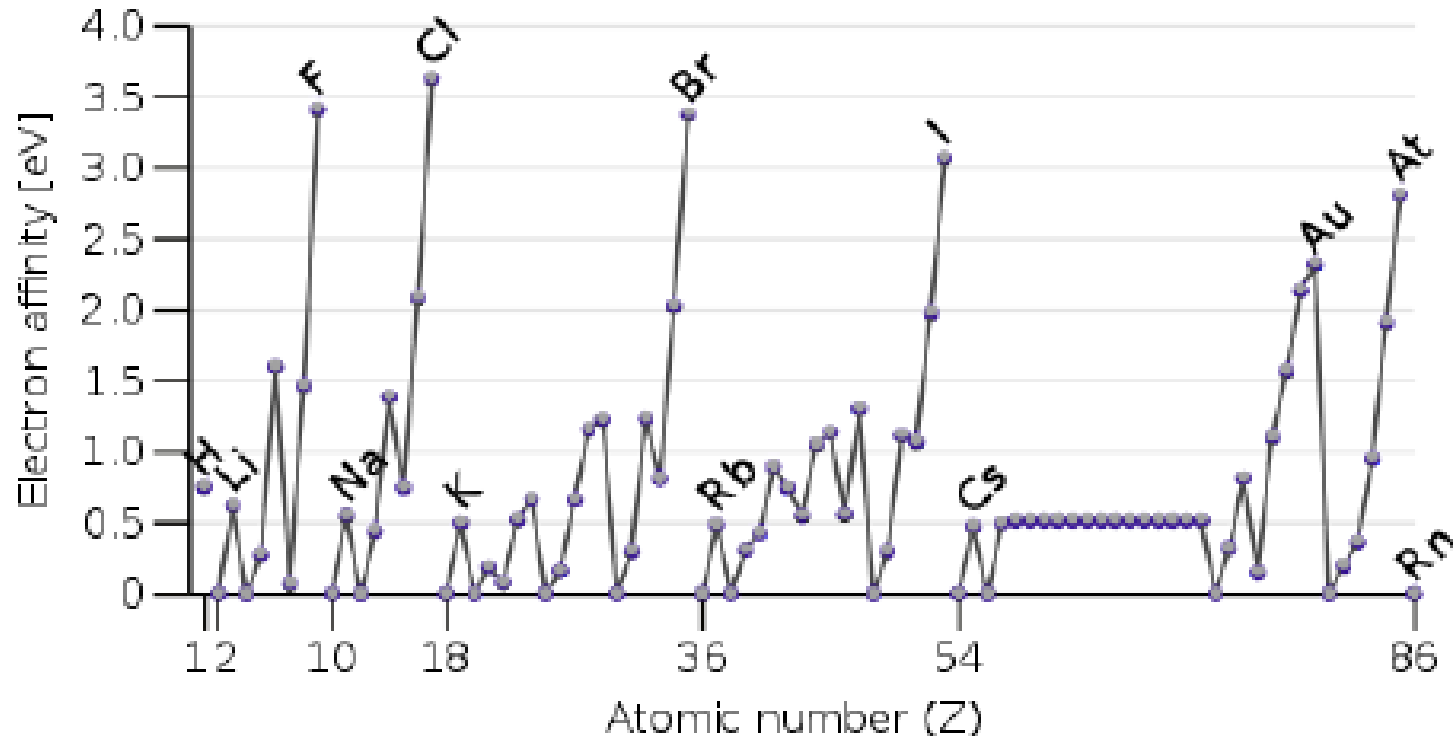
Ionization energy: each period begins at a minimum for the alkali metals, and ends at a maximum for the noble gases

Electronegativity is the tendency of an atom to attract a shared pair of electrons



Graph showing increasing electronegativity with growing number of selected groups

Electron affinity – the energy gained by forming a negative ion



- The lower these values – the more metallic the element is.

Effective potentials, screening, and alkali metals

- Recall: The valence electrons obey a single electron Schrodinger eqn. :

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}^l(r) \right) \psi = E \psi$$

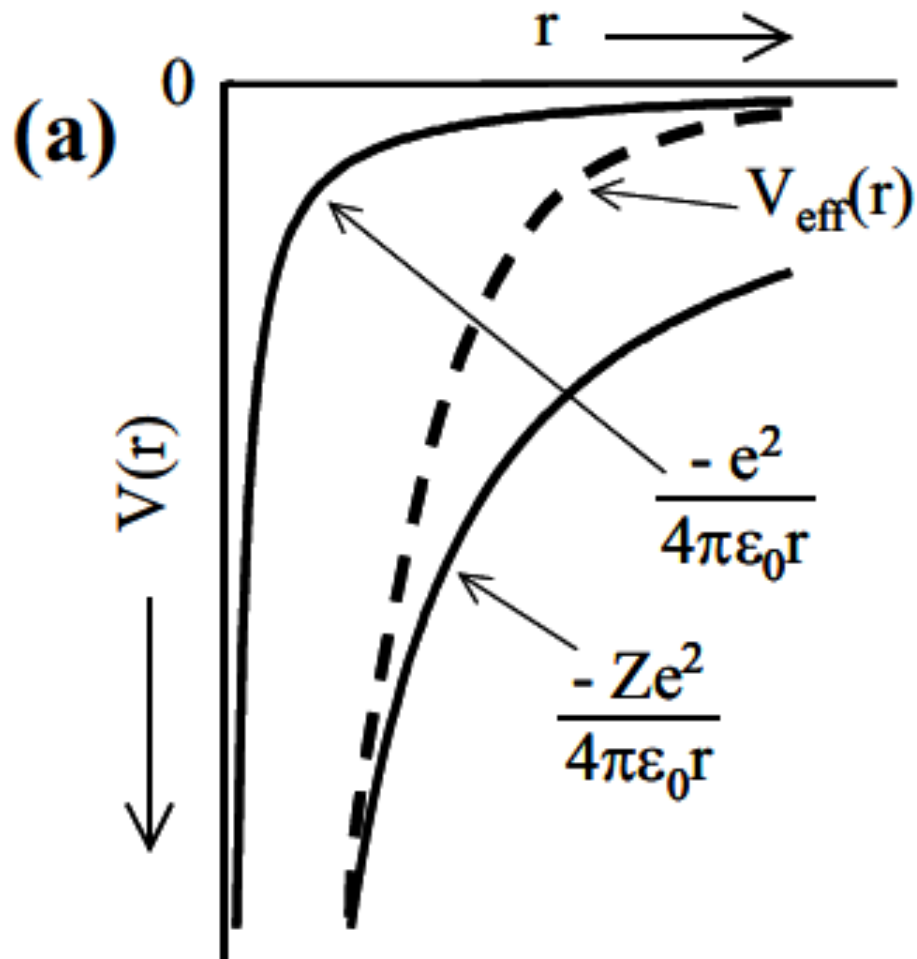
The nature of $V_{\text{eff}}(r)$:

In large distances the electron will feel $+e$

At small distances it will feel $+Ze$.

At medium distance, the potential will be in between.

The approximate potential:



The simplest multielectron atoms are the alkali metals

- Recall:

The energy of the electron level is:

$$E_n = - \left(\frac{Z}{n} \right)^2 R_H$$

In the case of the valence electron is should be:

$$E_n = -(1/n^2)R_H$$

- In practice: A quantum defect allows penetration of the inner shells by the valence electron.

Which gives the energy levels:

- Including the quantum defect:

$$E_{nl} = -\frac{R_H}{[n - \delta(l)]^2}$$

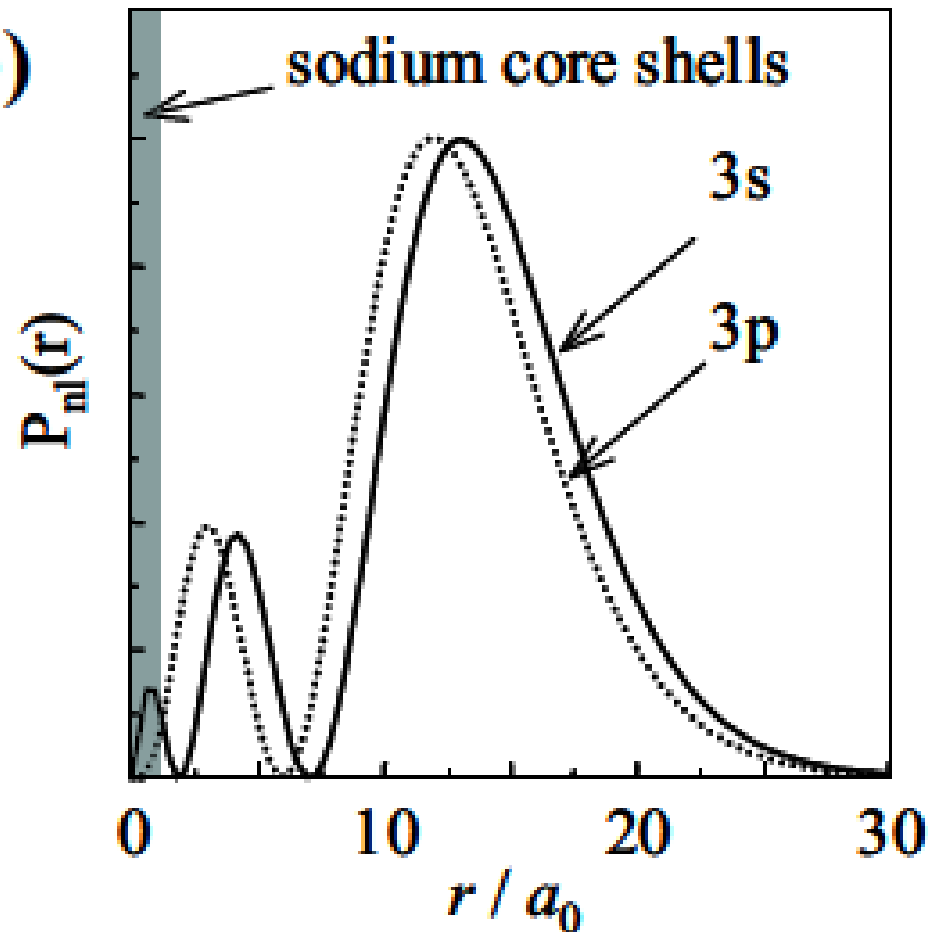
where $n \geq 3$ and $\delta(l)$ is the quantum defect.

- To understand why we Plot the radial probability densities of a hydrogenic atom with $Z=1$ of of 3s and 3p wavefunctions.
- This is a reasonable approximation for the valence electron.

There is a finite probability to penetrate the core level

- Plot in scale:
The 3s shows a larger penetration – demonstrates the dependence of σ on l .

(b)



σ depends largely on l (and less on n)

- The experimental results for σ in Na give:

l	$n = 3$	$n = 4$	$n = 5$	$n = 6$
0	1.373	1.357	1.352	1.349
1	0.883	0.867	0.862	0.859
2	0.010	0.011	0.013	0.011
3	—	0.000	-0.001	-0.008

Quantum defects can be used to calculate the emission spectrum

- Putting the values of the table:

$$\begin{aligned}\frac{hc}{\lambda} &= R_H \left(\frac{1}{[3 - \delta(3s)]^2} - \frac{1}{[3 - \delta(3p)]^2} \right) \\ &= (1.10 \times 10^5 \text{ cm}^{-1}) \times \left(\frac{1}{1.627^2} - \frac{1}{2.117^2} \right)\end{aligned}$$

- Giving a wavenumber and wavelength of yellow D line of Na (3p to 3s).

$$\bar{\nu} = 1.70 \times 10^4 \text{ cm}^{-1}, \quad 590\text{nm.}$$