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**

Quantum defect - Hydrogenic systems.

SP: 3.1, AP: 4.1 - 4.2. Exercises: 19 - 23 (**H6**)

Hydrogenic systems : "one electron outside filled orbitals"

Effective potential: $$V_{\text{eff}} = \frac{\hbar^2 \ell \cdot (\ell + 1)}{2\mu \cdot r^2} - \frac{Ze^2}{4\pi\varepsilon_0 \cdot r}$$

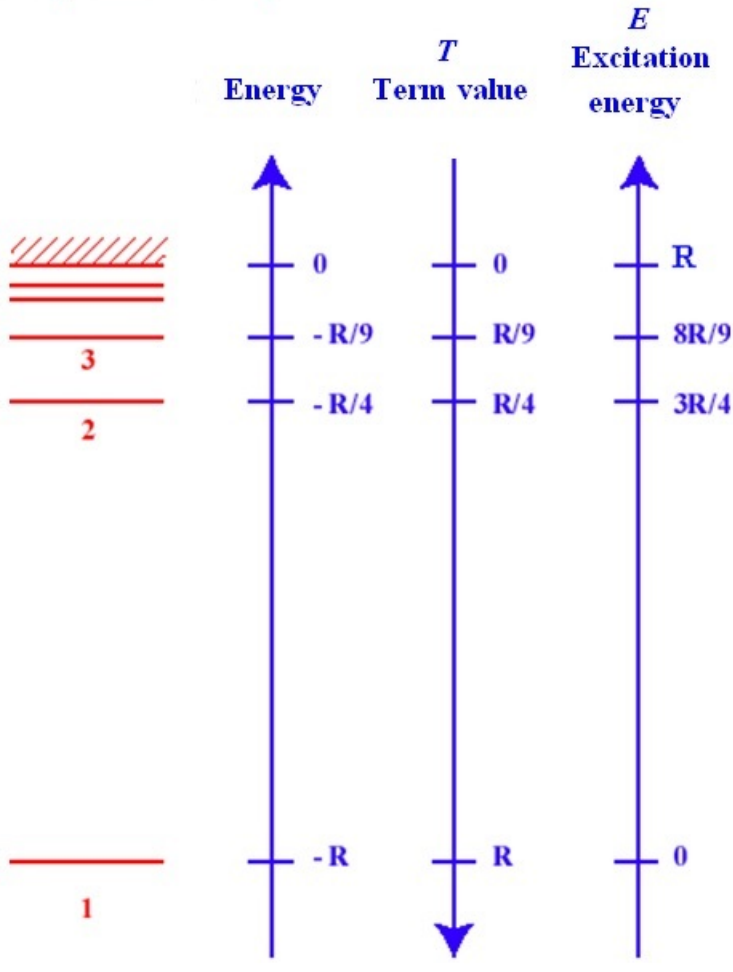
Term value or binding energy: $$T = R \cdot \frac{\zeta^2}{(n - \delta)^2}$$

Effective charge $\zeta = Z - N_{\text{iner}}$ and $\delta =$ quantum defect

δ is:

- experimentally determined
- strongly dependent of ℓ
- approximately independent of n.

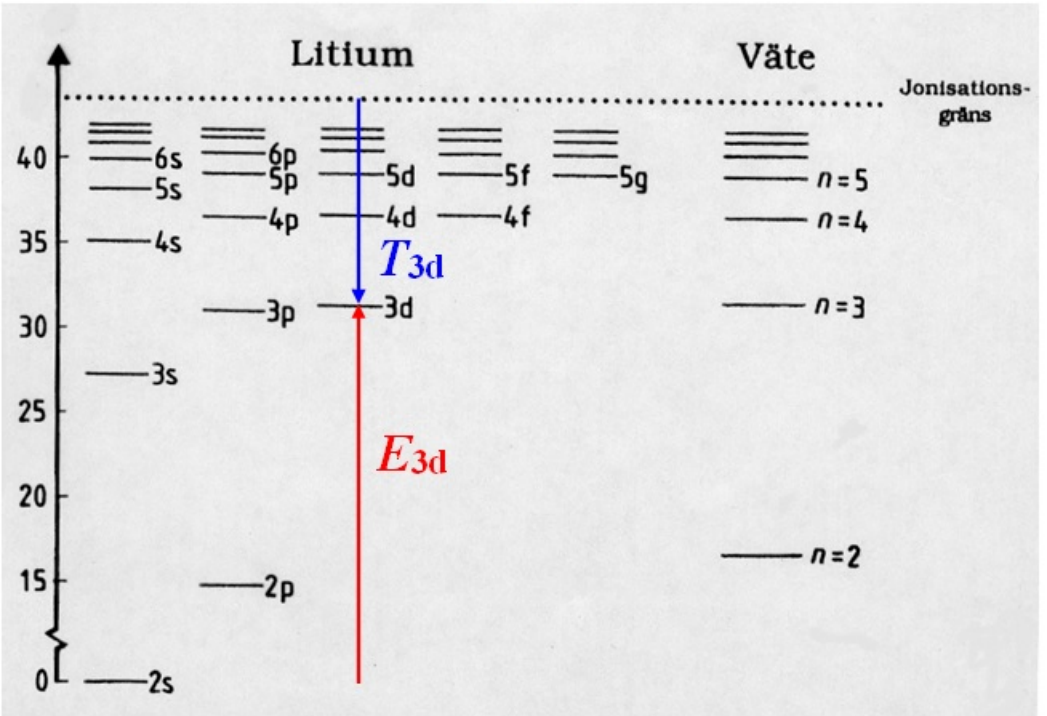
Energy scales (Values for H)



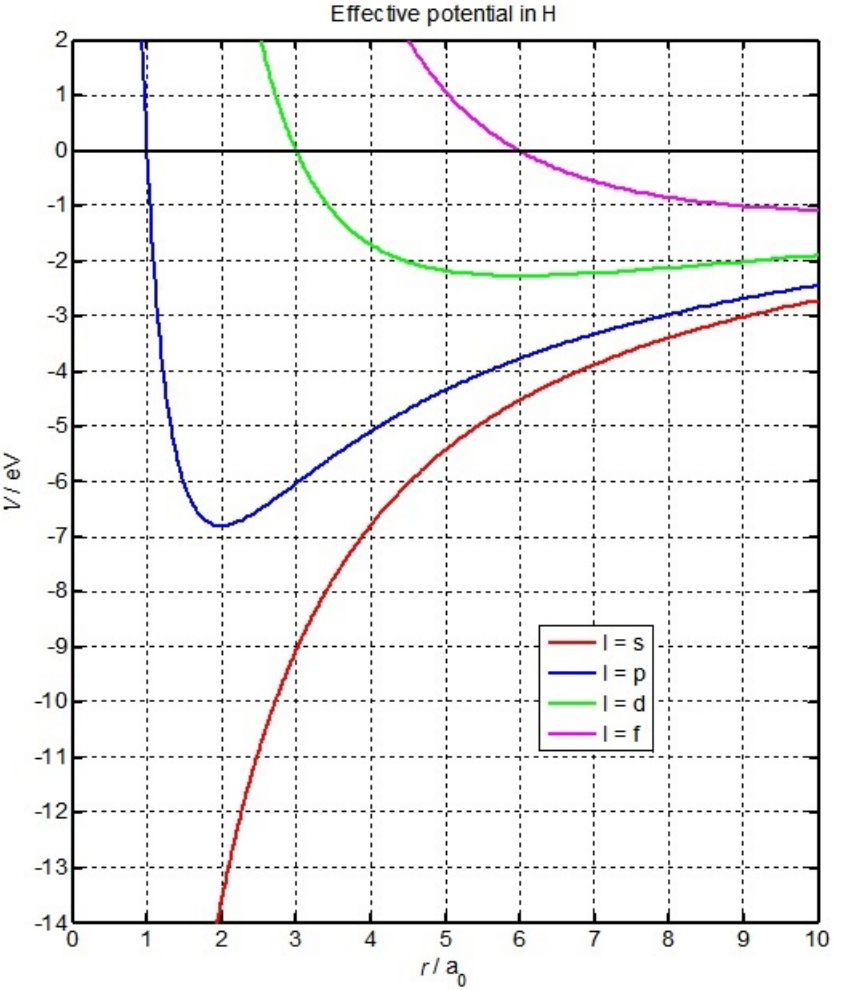
Term value = Binding energy. $T = E_{ion} - E$

Term values in Li and H.

$$T = E_{jon} - E$$



	T_{exp} / cm^{-1}	$T_H = \frac{1}{3^2} R_{Li}$ / cm^{-1}	% deviation
$1s^2 3s$	16281	12192	33
$1s^2 3p$	12562	-"-	3
$1s^2 3d$	12204	-"-	0.1



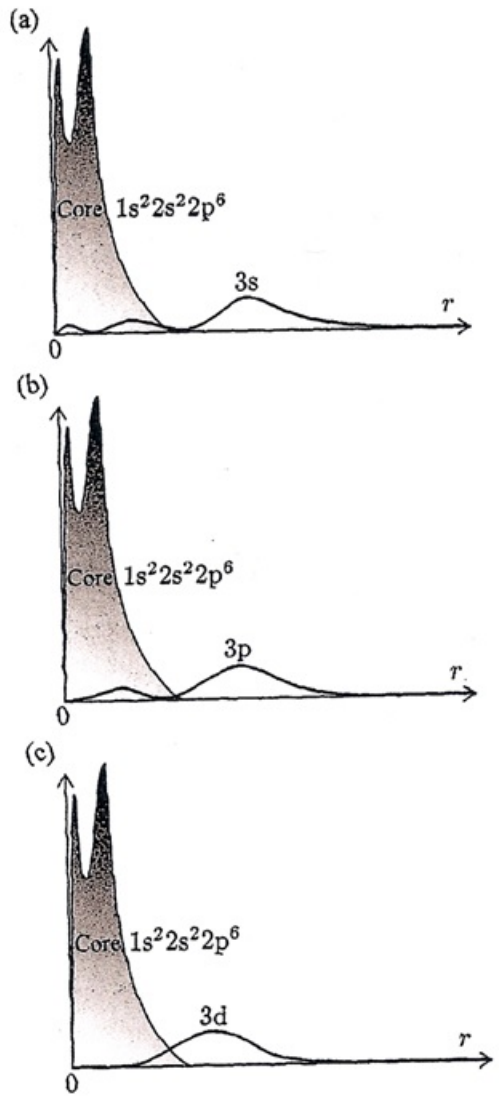
$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{L}^2}{2\mu \cdot r^2} - \frac{Ze^2}{4\pi\varepsilon_0 \cdot r}$$

$$V_{\text{eff}} = \frac{\hbar^2 \ell \cdot (\ell+1)}{2\mu \cdot r^2} - \frac{Ze^2}{4\pi\varepsilon_0 \cdot r}$$

Electrons with $\ell > 0$ are "pushed outwards by the centrifugal force"

Penetrating orbitals in Na

(Foot Fig 4.1)



Quantum defect in F VII

$$T = R \cdot \frac{Z^2}{n^2}$$ H-like

$$T = R \cdot \frac{\zeta^2}{n^2}$$ Completely screened nucleus

$$\zeta = Z - N_{\text{iner}}$$

$$T = R \cdot \frac{\zeta^2}{(n-\delta)^2}$$ δ = quantum defect

δ is:

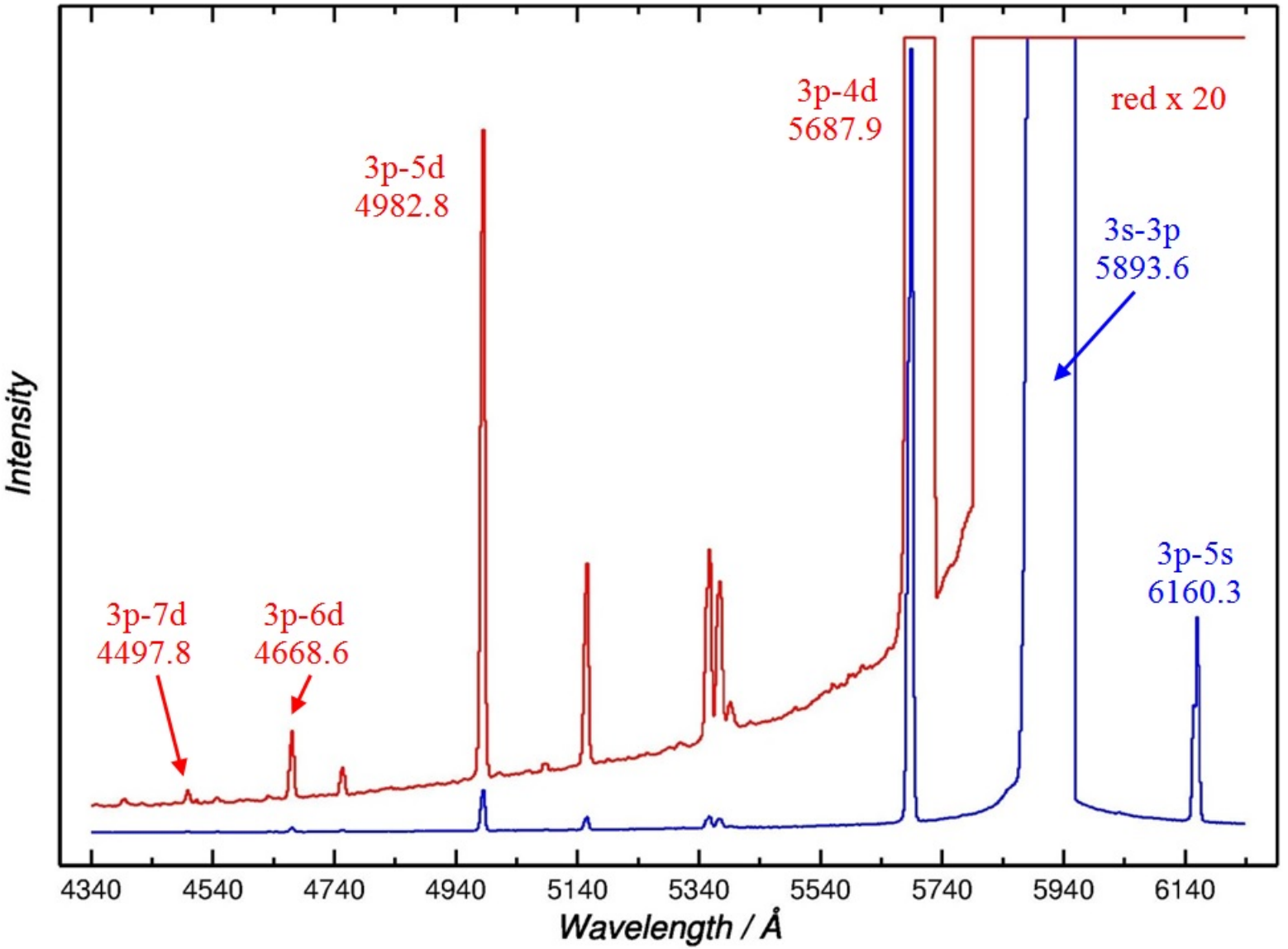
- experimentally determined
- strongly dependent of ℓ
- approximately independent of n.

Quantum defect in F VII (Li-like)

n	*s*	*p*	*d*	*f*	*g*
2	0.1026	0.02660			
3	0.0992	0.02693	0.001295		
4	0.0983	0.02711	0.001794	0.000262	
5	0.0979	0.02718	0.002030	0.000466	0.000181
6	0.0976	0.02782	0.002016	0.000529	0.000266
7	0.0975		0.002147	0.000455	-
8			0.002665	0.000528	0.000304
9				0.000530	

Engström, L., Physica Scripta 29, **113** (1984)

Na-spectrum


3p-4d
5687.9
red x 20
3p-5d
4982.8
3s-3p
5893.6
3p-5s
6160.3
3p-7d
4497.8
3p-6d
4668.6
Intensity
4340
4540
4740
4940
5140
5340
5540
5740
5940
6140
Wavelength / Å

Fine structure in the alkalis

H-like: $\Delta E_{SO} = R \cdot \dfrac{\alpha^2 Z^4}{n^3 \cdot \ell(\ell+1)}$. (Foot $2.56 + Z^4$ and in cm^{-1})

Alkali atoms: $\Delta E_{SO} = R \cdot \dfrac{\alpha^2 \zeta^4}{(n^*)^3 \cdot \ell(\ell+1)}$. $\zeta = Z - N_{\text{inner}}$, $n^* = n - \delta_\ell$

Note. Can't be used for quantitative calculations but very accurate for scaling from one n to another. For example:

$$\frac{\Delta E(3p)}{\Delta E(2p)} = \frac{(2^*)^3}{(3^*)^3} \Rightarrow \Delta E(3p) = \Delta E(2p) \cdot \frac{(2-\delta)^3}{(3-\delta)^3}$$