

Periodic table

Recall;  $H = H_c + H_1$  ;  $H_c \Psi_c = E_c \Psi_c$

$\sum_{i=1}^N \left( -\frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 + V(\vec{r}_i) \right)$ 

 $\uparrow$  central  
 $\downarrow$  perturb.
 

 $\underbrace{\quad}_{\sum_i E_i}$

$$\Psi_c(r_1, r_2, \dots, r_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \psi_\alpha(r_1) \psi_\beta(r_2) \dots \psi_\nu(r_N)$$

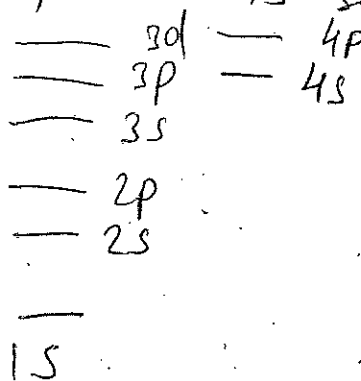
$$u_{n\ell m_\ell m_s}(r) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \chi_{\frac{1}{2}, m_s}$$

permutation of electron coordinates

$$-\frac{1}{2} \left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} \right] R_{n\ell}(r) + V(r) R_{n\ell}(r) =$$

If  $V(r) = -\frac{Ze^2}{r} \Rightarrow E_n \uparrow$  as  $n \uparrow$  =  $E_{n\ell} R_{n\ell}(r)$

If  $V(r)$  is something else  $\Rightarrow E_{n\ell} \uparrow$  as  $n+l \uparrow \Rightarrow$



Note:  $E_{4s} < E_{3d}$

4+0 3+2

atomic number  $\uparrow$   
 $Z$ : nuclear charge  $\downarrow$

ground state of neutral atoms:  $Z$  electrons occupy the lowest individual energy levels

Valence electrons; those in the sub-shell of highest energy  
less tightly bound

Electron configuration: filling up shells

	K-shell (n=1)	Z	L-shell (n=2)	M-shell (n=3)
(H)	1s	2		
(He)	1s <sup>2</sup>	2		
		3	(Li) 1s <sup>2</sup> 2s	11 (Na) [Ne] 3s
		4	(Be) 1s <sup>2</sup> 2s <sup>2</sup>	18 (Ar) [Ne] 3s <sup>2</sup> 3p <sup>6</sup>
		5	(B) 1s <sup>2</sup> 2s <sup>2</sup> 2p	
		10	(Ne) 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	

Then, since  $E_{4s} < E_{3d}$

19 (K)	[Ar] 4s
20 (Ca)	[Ar] 4s <sup>2</sup>
21 (Sc)	[Ar] 4s <sup>2</sup> 3d
29 (Cu)	[Ar] 4s 3d <sup>10</sup>

24 (Cr) [Ar] 4s 3d<sup>5</sup>  
 25 (Mn) [Ar] 4s<sup>2</sup> 3d<sup>5</sup>

first transition (or iron) group  
 competition in filling energy levels, since  $E_{4s} \sim E_{3d}$

Second transition group: (Z = 39 to 48)  $\Leftrightarrow$  n = 4  
 (or palladium)

Third — — — — — : (Z = 71 to 80)  $\Leftrightarrow$  n = 5  
 (or platinum)

Rare-earth elements: (Z = 57 - 70)  $\Leftrightarrow$  4f vs 5d  
 (lanthanides)

Actinides (Z = 89 - 102)  $\Leftrightarrow$  5f vs 6d

competition  $\rightarrow$   
 between nd and (n+1)s

Ionization potential  $\Rightarrow$  non-monotonic in  $Z$  (3)

(in contrast to  $(H)$ -like ions!)

Maximum at full shells (noble gases - He, Ne, Ar, Kr, Xe, Rn)  
Smallest for alkalis (Li, Na, K, Rb, Cs, Fr)  
↑ Chemically reactive  $\rightarrow$  1 valence electron  
↑ Chemically inert

halogens (F, Cl, Br, I)  $\leftarrow$  1 electron missing to fill the shell completely

Note: all of this is due to the Pauli exclusion principle (otherwise all electrons would be in 1s state, and all atoms would be alike)

So, how do we calculate energies?  $\Rightarrow$  need  $V(r) \Rightarrow$

know that at  $r \rightarrow 0$   $V(r) \rightarrow -\frac{Ze^2}{4\pi\epsilon_0 r}$

$r \rightarrow \infty$   $V(r) \rightarrow -\frac{e^2}{4\pi\epsilon_0 r}$  (neutral atom)

intermediate  $r$

$V(r) = ?$

$\rightarrow$  Hartree-Fock; self-consistent field

Thomas-Fermi:

find  $V(r)$   $\Leftarrow$  N-electron atom as a Fermi electron gas confined by  $V(r)$   
↑  
 $\rho(r)$   
↑  
electron density

