Complex atoms and the Periodic System of the elements

Non-central forces due to electron repulsion

Central field approximation \rightarrow electronic orbitals \rightarrow lift degeneracy of l

$$E_{n\ell} = -\frac{R(hc)}{(n-\delta_{\ell})^2}$$

🌠 MA-Table (Perodic System of Elements)																	
1 _H	1																² He
³ Li	⁴ Be			1	3.31 k	eV						⁵ B	⁶ C	⁷ N	⁸ 0	⁹ F	¹⁰ Ne
¹¹ Na	¹² Mg			Ove	rlap (+- 70 eV) with all lines				¹³ AI	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ Cl	¹⁸ Ar			
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
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	⁵⁴ Xe
⁵⁵ Cs	⁵⁶ Ba	57 La	72 Hf	⁷³ Та	⁷⁴ W	75 Re	⁷⁶ Os	⁷⁷ lr	⁷⁸ Pt	⁷⁹ Au	80 Hg	⁸¹ TI	⁸² Pb	⁸³ Bi	84 Po	⁸⁵ At	⁸⁶ Rn
⁸⁷ Fr	88 Ra	⁸⁹ Ac	104 Ku	¹⁰⁵ Bo												[9
	K-overlaps 58 59 60 61 L-overlaps Ce Pr Nd Pm				62 Sm	63 Eu	64 Gd	65 Tb	66 Dv	67 Ho	68 Er	⁶⁹ Tm	70 Yb	71 Lu			
(c) m	M-overlaps (c) microanalystnet			⁹⁰ Th	91 Pa	92 U	93 Np	⁹⁴ Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 ∭d	102 No	103 ЦГ

→ "Aufbau" principle

Complex atoms and the central field approximation



CFA:
The overall effect of
$$V\left(\sum_{i} \vec{r_i}\right)$$

is centrally directed toward the nucleus
 $-\frac{Ze^2}{4\pi\varepsilon_0 r}$ for $r \to 0$

$$\longrightarrow V_c(r) \xrightarrow{-\frac{Ze^-}{4\pi\varepsilon_0 r}} \text{for } r \to 0$$

$$-\frac{e^2}{4\pi\varepsilon_0 r} \text{ for } r \to \infty$$

Then V can be written in terms of an "effective screened nuclear charge"

$$V_{cfa}(r) = -\frac{Z_{eff}(r)e^2}{4\pi\varepsilon_0 r}$$

Note:
$$V_{atom} = V_{cfa}(r) + V_{ee'}^{NC}$$

Separation of variables in the central field approximation

Product wave function

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_Z) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)\cdots\psi_Z(\vec{r}_Z)$$

Potential and eigenenergy

$$V = \sum_{i=1}^{Z} V_c(r_i) \qquad E = \sum_{i=1}^{Z} E_i$$

Insertion of trial yields a set of equations:

 $-\frac{\hbar^2}{2m}\nabla_i^2\Psi(\vec{r}_i) + V_c(r_i)\Psi(\vec{r}_i) = E_i\Psi(\vec{r}_i)$

The potential function is not Coulombic i.e. is *not* 1/r but $\underline{Z_{eff}(r)}$

1. Angular part of the wave function is the same, hence angular functions

 $\mathbf{Y}_{l_i m_i}(\theta_i, \phi_i)$



→ Energy E_{nl} depends on ℓ Energy E_{nl} does *not* depend on *m*

Wave functions for single "orbital"

$$\psi_i(\vec{r}_i) = R_{nl}(r_i) Y_{l_i m_i}(\theta_i, \phi_i) \uparrow \downarrow \rangle$$



Screening in the central field approximation



For low ℓ values (and same n) electron comes closer to the nucleus

More Coulomb attraction

More binding energy

Lower ℓ states \rightarrow lower energy





Screening in the central field approximation



For low ℓ values (and same n) electron comes closer to the nucleus

More Coulomb attraction

More binding energy

Lower ℓ states \rightarrow lower energy





Lowering of low ℓ quantum states as an effect of screening





Screening and the quantum defect



Levels described with:

$$E_{nl} = -\frac{R_{Na}}{(n - \delta_\ell)^2}$$

With quantum defects:

 $δ_s = 1.35$ $δ_p = 0.86$ $δ_d = 0.01$ $δ_f = 0.00$

Lecture Notes Structure of Matter: Atoms and Molecules; W. Ubachs

Aufbau principle for multi-electron atoms

Eigenfunctions in multi-electron atom $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_Z) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \dots \psi_Z(\vec{r}_Z)$

1) Electrons fill the one-electron orbitals $\psi_i(\vec{r}_i) = R_{nl}(r_i) Y_{l_i m_i}(\theta_i, \phi_i) \uparrow \downarrow \rangle$

into a "configuration":

$$\left[\prod_{i} \psi_{i}(\vec{r}_{i}) \right]$$

- 2) Pauli principle dictates: single occupancy
- 3) For filled shells

$$\sum_{shell} m_{\ell_i} = 0 \Longrightarrow \vec{L}_{tot} = 0$$

$$\sum_{shell} s_{\ell_i} = 0 \Longrightarrow \vec{S}_{tot} = 0$$
shell

Degeneracy $2n^2$ structures the Periodic System



Note:

this is about ground states of the atoms

Lecture Notes Structure of Matter: Atoms and Molecules; W. Ubachs

Ground state orbital configurations for multi-electron atoms

Noble gases

He configuration $(1s)^2$; term ${}^{1}S_0$ Ne conf. $(1s)^2(2s)^2(2p)^6$; term ${}^{1}S_0$ Ar conf. $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$

<u>Alkali metals</u>

Li $(1s)^2(2s)$ term ${}^2S_{1/2}$ Na $(1s)^2(2s)^2(2p)^6(3s)$ term ${}^2S_{1/2}$ K $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)$

Earth alkali metals

Mg
$$(1s)^2(2s)^2(2p)^6(3s)^2$$
 term ${}^{1}S_0$
Ca $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2$



Binding energies of the one-electron orbitals vary with Z: Screening effects

Irregularities and degeneracies

Transition metals; effect of 3d orbitals:

 $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2$ Ca $(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)^{2}(3d)$ Sc $(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)^{2}(3d)^{2}$ Ti $(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)^{2}(3d)^{3}$ V $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)(3d)^5$ Cr $(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)^{2}(3d)^{5}$ Mn $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^6$ Fe $(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)^{2}(3d)^{7}$ Со $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^8$ Ni $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)(3d)^{10}$ Cu $(1s)^{2}(2s)^{2}(2p)^{6}(3s)^{2}(3p)^{6}(4s)^{2}(3d)^{10}$ Zn

ground term $^{1}S_{0}$ $^{2}D_{3/2}$ $^{3}F_{2}$ ${}^{4}F_{3/2}$ ⁷S₃ ⁶S_{5/2} ⁵D₄ ${}^{4}F_{9/2}$ ³F₄ ${}^{2}S_{1/2}$

 ${}^{1}S_{0}$

Near degeneracy of *3d* and *4s* orbitals

Competition in allocation of electrons

Ionization Potentials vary over the periodic structures



-Shell closing for the noble gases;

-Alkali metals outer electron least binding enegy



Alkali atoms

Angular momentum coupling

$$\vec{L} = \vec{\ell}_1 + \vec{\ell}_2 + \dots + \vec{\ell}_z$$
$$\vec{S} = \vec{s}_1 + \vec{s}_2 + \dots + \vec{s}_z$$
$$\vec{J} = \vec{L} + \vec{S}$$

$$M_{L} = m_{\ell_{1}} + m_{\ell_{2}} \dots + m_{\ell_{z}}$$
$$M_{S} = m_{s_{1}} + m_{s_{2}} \dots + m_{s_{z}}$$

Filled shells have $\vec{L} = \vec{S} = 0$

¹S₀ state

Filled shells: spherical charge distribution

 $V_{CFA}(r)$ is OK

Alkali = hydrogenlike with $Z_{eff} \sim 1$ $V_{SL} = \frac{Ze^2}{4\pi\varepsilon_0} \frac{\vec{S} \cdot \vec{L}}{2m^2c^2r^3}$ with $\vec{S} \cdot \vec{L} = \frac{1}{2} \left(J^2 - L^2 - S^2\right)$

Selection rules: $\Delta \ell = \pm 1$ $\Delta j = 0, \pm 1$

 $\Delta s = 0$



Deviation from central field approximation

$$V_{ee}' = -\frac{Ze^2}{4\pi\varepsilon_0} \sum_{i=1}^{Z} \frac{1}{\left|\vec{r}_i\right|} + \frac{e^2}{4\pi\varepsilon_0} \sum_{i< j} \frac{1}{\left|\vec{r}_i - \vec{r}_j\right|} - V_c(r_i)$$

 V_{ee} ' represents the non-central forces

Causes a distinction between

$$\left|\Psi_{-}(ec{r_{i}})
ight|^{2}$$
 and $\left|\Psi_{+}(ec{r_{i}})
ight|^{2}$

Similar is in case of He

 $\Psi_{-}^{space}(\vec{r}_i)$ has lower energy



Hund rule (1): States of highest multiplicity have lowest energy





Empirical, but some semi-classical argument Higher L composed of highest m_l , so less overlap



Hund rule (3): Ordering of spin-orbit states

$$\left\langle V_{SL} \right\rangle = \left\langle \sum_{i} \xi(r_i) \vec{S}_i \cdot \vec{L}_i \right\rangle = A \left\langle \vec{S} \cdot \vec{L} \right\rangle = \frac{A\hbar^2}{2} \left[j(j+1) - \ell(\ell+1) - s(s+1) \right]$$

For: $j=j_{max}=l+s$ $\langle V_{SL}\rangle = A\hbar^2\ell s$ If A>O high J up

Spin-orbit inversion for less than half filled shell

$$\langle V_{SL} \rangle = \left\langle \sum_{electrons}^{n} \xi(r_i) \vec{S}_i \cdot \vec{L}_i \right\rangle = \left\langle \sum_{electrons}^{N} \xi(r_i) \vec{S}_i \cdot \vec{L}_i - \sum_{holes}^{N-n} \xi(r_i) \vec{S}_i \cdot \vec{L}_i \right\rangle = \left\langle -\sum_{holes}^{N-n} \xi(r_i) \vec{S}_i \cdot \vec{L}_i \right\rangle$$

inversion for less than half filled shell
A>0
A>0
A<0
So A=0 for half-filled shell
Why A<0?
Holes do the job (positive charge)

Example: structure of the carbon atom

Z=6 : Ground state configuration

 $(1s)^{2}(2s)^{2}(2p)^{2}$

Excited states: (1s)²(2s)²(2p)(3s) (1s)²(2s)²(2p)(3p), etc

Angular momenta for the $(2p)^2$ configuration

 $\ell_1 = 1, s_1 = \frac{1}{2} \qquad \qquad \vec{L} = \vec{\ell}_1 + \vec{\ell}_2 = 0, 1, 2$ $\ell_2 = 1, s_2 = \frac{1}{2} \qquad \qquad \vec{S} = \vec{s}_1 + \vec{s}_2 = 0, 1$ So possible terms:

¹S₀ (1) ¹P₁ (3) ¹D₂ (5) ³S₁ (3) ³P_{0,1,2} (9) ³D_{1,2,3} (15) 36 states

$$\left\{ \ell = 1, s = \frac{1}{2} \right\} \otimes \left| \ell' = 1, s' = \frac{1}{2} \right\}$$

= 36space

But this does not yet include the Pauli exclusion principle

Lecture Notes Structure of Matter: Atoms and Molecules; W. Ubachs

Sort out what substates exist for the $(2p)^2$ configuration

			Ms			
		1	0	-1		
	2	1+1+	1+1- 1-1+	1-1-		
	1	1+0+	1+0- 0+1-	1-0-		
		0+1+	1-0+ 0-1+	0-1-		
ML	0	1*-1* O*O* -1*1*	1+ -1- 11+ -1+ 11- 1+ 0+0- 0-0+	1 ⁻ -1 ⁻ -1 ⁻ 1 ⁻ 0 ⁻ 0 ⁻		
	-1	-1*0* 0* -1*	-1+0- 0+ -1- -1-0+ 01+	-1-0- 01-		
	-2	-1+ -1+	-1+ -1- -11+	-11-		

Write $(m_l)^{m_s}$



Sort out what substates exist for the $(2p)^2$ configuration; invoke the Pauli principle

			Ms			
		1	0	-1		
ML	2	1+1+	1+1- 1-1+	1-1-		
	1	1+0+	1+0- 0+1-	1-0-		
	T	0+1+	1-0 + 0-1+	0-1-		
	0	1*-1* O*O* -1*1*	1+ -1- 11+ -1+ 11- 1+ 0+0- 0-0+	1 ⁻ -1 ⁻ -1 ⁻ 1 ⁻ 0 ⁻ 0 ⁻		
	-1	-1+0+ O+ -1+	-1+0- 0+ -1- -1-0+ 01+	-1-0- 01-		
	-2	-1+ -1+	- 1+ -1 - -11+	-11-		

Write $(m_l)^{m_s}$



Sort out what substates are allowed by the Pauli principle



Write $(m_l)^{m_s}$

1. State with the highest $M_{\rm S}$ $M_{\rm S}$ =1

So there is a state with S=1

Highest M_L =1, so there exists a state with L=1

So ³P is a Pauli allowed state





 $^{1}\mathsf{D}_{2}$



Ground state <u>configuration</u> of the Carbon atom

