Complex Atoms; The Exclusion Principle and the Periodic System

In order to understand the electron distributions in atoms, another principle is needed. This is the Pauli exclusion principle:

No two electrons in an atom can occupy the same quantum state.

The quantum state is specified by the four quantum numbers; no two electrons can have the same set.





Wolfgang Pauli

The Nobel Prize in Physics 1945 "for the discovery of the Exclusion Principle, also called the Pauli Principle" Question 1: why can we use 1-electron orbitals in this problem Question 2: why do *I*-values for the same *n* have differing energies

The potential energy in a multi-electron atom:

$$V = -\frac{Ze^{2}}{4\pi\varepsilon_{0}}\sum_{i=1}^{Z}\frac{1}{|\vec{r}_{i}|} + \frac{e^{2}}{4\pi\varepsilon_{0}}\sum_{i
attraction to nucleus repulsion between electrons$$

V is a *non*-central potential

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

is centrally directed toward the nucleus



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

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

This is a central potential !!

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

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

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 $Z_{e\!f\!f}(r)$

r

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

2. Radial part of the wave function

$$-\frac{\hbar^2}{2mr}\frac{d}{dr}rR_{nl} + \left[\frac{Z_{eff}(r)}{r} + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]R_{nl} = E_{nl}R_{nl}$$

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

Wave functions for single "orbital"

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

Radial part of the wave function $-\frac{\hbar^{2}}{2mr}\frac{d}{dr}rR_{nl} + \left[\frac{Z_{eff}(r)}{r} + \frac{\hbar^{2}\ell(\ell+1)}{2mr^{2}}\right]R_{nl} = E_{nl}R_{nl}$ $\longrightarrow \text{ Energy } E_{nl} \text{ depends on } \ell$ $\text{ Energy } E_{nl} \text{ does not depend on } m$



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

More Coulomb attraction

More binding energy

Wave functions for single "orbital" $\psi_i(\vec{r}_i) = R_{nl}(r_i) Y_{l_i m_i}(\theta_i, \phi_i) \uparrow, \downarrow \rangle$



s-states have higher density near the nucleus

Lowering of low ℓ quantum states as an effect of screening



Complex Atoms; the Aufbau Principle

This chart shows the occupied – and some unoccupied – states in He, Li, and Na.



The Periodic Table of the Elements

TABLE 39–2 Ground-State Quantum Numbers				
Helium, $Z = 2$				
n	l	m _l	m _s	
1	0	0	$\frac{1}{2}$	
1	0	0	$-\frac{1}{2}$	
Lithium, $Z = 3$				
n	l	m _l	m _s	
1	0	0	$\frac{1}{2}$	
1	0	0	$-\frac{1}{2}$	
2	0	0	$\frac{1}{2}$	
Sodium, $Z = 11$				
n	l	m _l	m _s	
1	0	0	$\frac{1}{2}$	
1	0	0	$-\frac{1}{2}$	
2	0	0	$\frac{1}{2}$	
2	0	0	$-\frac{1}{2}$	
2	1	1	$\frac{1}{2}$	
2	1	1	$-\frac{1}{2}$	
2	1	0	$\frac{1}{2}$	
2	1	0	$-\frac{1}{2}$	
	1	0	2	
2	1	-1	$\frac{1}{2}$	
2 2	1 1 1	-1 -1	$\frac{\frac{1}{2}}{-\frac{1}{2}}$	

Each value of ℓ is given its own letter symbol.

Electron configurations are written by giving the value for n, the letter code for ℓ , and the number of electrons in the subshell as a superscript.

For example, here is the groundstate configuration of sodium:

 $1s^2 2s^2 2p^6 3s^1$

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The Periodic Table of the Elements

TABLE 39–3 Value of ℓ			
Value of <i>l</i>	Letter Symbol	Maximum Number of Electrons in Subshell	
0	S	2	
1	р	6	
2	d	10	
3	f	14	
4	g	18	
5	h	22	
:	•	• •	

subshells

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Aufbau principle for multi-electron atoms

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

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": $\prod_i \psi_i(\vec{r}_i)$

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 <u>ground</u> states of the atoms

Electron spin and the atom

Additional quantum number

 $|nlm\rangle \rightarrow |nlsm_lm_s\rangle$

Wave functions

 $\Psi_{nlm}(\vec{r},t) = R_{nl}(r) Y_{lm}(\theta,\phi) e^{-iE_n t/\hbar} |\uparrow,\downarrow\rangle$

No effect on energy levels, except for magnetic coupling to other angular momenta

Degeneracy

$$\frac{2(2\ell+1)}{2n^2}$$



Selection rules

S is not a spatial operator, so no effect on dipole selection rules

Ground state orbital configurations for multi-electron atoms

Noble gases

He configuration $(1s)^2$; closed shell Ne conf. $(1s)^2(2s)^2(2p)^6$; closed shell Ar conf. $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$; closed shell

<u>Alkali metals</u>

Li $(1s)^2(2s)$ one open shell electron Na $(1s)^2(2s)^2(2p)^6(3s)$ one open shell electron K $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)$

Earth alkali metals

Mg
$$(1s)^2(2s)^2(2p)^6(3s)^2$$
 closed
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





🌠 MA-Table (Perodic System of Elements)

